INTERACTION OF OXYGEN
WITH HYDROGEN SULPHIDE ON A Ni/Al$_2$O$_3$ CATALYST*

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Interaction of oxygen at 20°C with hydrogen sulphide presorbed at 55°C and *vice versa* has been investigated. Different temperatures of adsorption of oxygen and of hydrogen sulphide were chosen since approximately the same number of sulphur and oxygen atoms were adsorbed on a clean surface at the mentioned temperatures. The characteristics of the interaction changed with changing the sequence of the gases adsorbed. When oxygen was adsorbed on a catalyst with preadsorbed hydrogen sulphide the adsorbed amount was the same as that on a clean catalyst. This interaction was not followed by any release of water into the gaseous phase. When hydrogen sulphide was adsorbed on a catalyst with presorbed oxygen a reaction took place yielding water. The amount of sorbed hydrogen sulphide was under identical conditions up to twice as high as on a clean catalyst surface. On the surface of a catalyst on which subsequently hydrogen sulphide and oxygen were adsorbed at 55° and 20°C, respectively, further amount of hydrogen sulphide is sorbed under the formation of water.

Interaction of chemisorbed hydrogen sulphide and oxygen has hitherto not been studied on nickel catalysts. Up to now, attention has been paid to oxygen sorption on a nickel sulphide catalyst at room temperature[1]. Delafosse and coworkers[2] studied the reaction of oxygen with hydrogen sulphide on NiS$_2$ at 170°C. Interaction of hydrogen selenide with chemisorbed oxygen on nickel was studied by Al-Haidery and coworkers[3]. These authors found that presorbed oxygen enhances the amount of the subsequently adsorbed hydrogen selenide.

In the present paper consecutive adsorptions of oxygen and hydrogen sulphide were investigated with the aim to elucidate the course and mechanism of their mutual interactions.

EXPERIMENTAL

Adsorption of hydrogen sulphide and oxygen was measured in a vacuum apparatus with quartz helices, as described in our previous paper[4]. Weight changes during adsorption were determined from the extension of quartz helices (75 windings, wire diameter 300 nm) read off by means of

a cathetometer KM 6 (USSR). Adsorption of oxygen was measured at 20°C, that of hydrogen sulphide at 55°C. In this case of interaction of oxygen with the surface of the catalyst with presorbed hydrogen sulphide, the amount adsorbed could be determined directly. However, when hydrogen sulphide interacts with presorbed oxygen, water is formed which has desorbed into the gaseous phase and was then condensed in the protecting freezing trap, placed before the catalyst and immersed in a bath of solid carbon dioxide in ethanol. To determine the amount adsorbed it was necessary to find the amount of the desorbed water and, on the basis of mass balance, to carry out the corresponding correction. The amount of the released and condensed water was determined from the tension of the water vapour after removing the bath from the freezing trap and after tempering the measuring volume. At the same time, also the weight increase of the catalyst had to be determined because a part of the water vapour was readsorbed on the catalyst.

Catalyst Ni/Al_2O_3 was prepared similarly as in the previous paper[4] by precipitation from the solutions of nickel nitrate and sodium aluminate. The precipitate was washed, dried and calcinated and then pressed into tablets with graphite added. Afterwards the catalyst was reduced in hydrogen at 425°C and after cooling was passivated by controlled oxygen chemisorption at room temperature. Prior to measurement the passivated catalyst was again reduced with hydrogen at 350°C for 25 h. After reduction the sample was evacuated to pressure of 10^{-4} Torr at 350°C. The catalyst in the reduced state contained 57·8 w % of Ni.

Hydrogen, taken from steel flasks, was first dried, then freed from oxygen by passing over Deoxo catalyst and then dried over calcium chloride. Oxygen of medicinal purity was taken from steel flask and purified by passing through a drying tower with calcium chloride and potassium hydroxide. Hydrogen sulphide was prepared by reaction of sodium sulphide with 10% sulphuric acid[4]. The gas was dried with calcium chloride, passed through freezing traps immersed in a bath of solid carbon dioxide in ethanol and its final purification was performed by repeated evacuation of the gas solidified in liquid nitrogen.

RESULTS

The results of separate adsorption of oxygen and hydrogen sulphide on the catalyst Ni/Al_2O_3 were described in our previous paper[4]. Total surface area of the reduced catalyst was 170 m²/g (as determined by the BET method using argon). Using the method of selective oxygen chemisorption the number of surface active centers of nickel was found to be $10\cdot2 . 10^{20}$ per 1 g of the reduced catalyst. All values of the adsorbed amount given further are related to 1 g of the reduced catalyst.

Interaction of oxygen with presorbed hydrogen sulphide. Hydrogen sulphide was adsorbed on the reduced catalyst after evacuation in portions $(2-5 . 10^{20}$ molecules) at 55°C. After evacuation of the gaseous phase and changing the temperature from 55°C to 20°C oxygen was admitted. During its adsorption no oxygen was released into the gaseous phase. Oxygen was bound irreversibly on the catalyst. On the average $10\cdot5 . 10^{20}$ oxygen molecules were adsorbed which is practically identical with the value found on clean catalyst surface. Heating the catalyst after oxygen adsorption to 150°C caused no desorption which indicates that all components are very strongly bound to the catalyst.

Interaction of hydrogen sulphide with presorbed oxygen. Oxygen was admitted in portions $(1 . 10^{20}$ molecules) on the reduced catalyst after evacuation at 20°C.

After adsorption (10·2 . 10^{20} molecules) and evacuation the temperature was changed from 20°C to 55°C and hydrogen sulphide was admitted in portions. Adsorption of hydrogen sulphide on a clean catalyst surface proceeds completely to the state when c. 2 . 10^{20} hydrogen sulphide molecules are adsorbed on the catalyst[4]. Further adsorption was already accompanied by the evolution of a gradually growing amount of hydrogen into the gaseous phase. When hydrogen sulphide is adsorbed on the catalyst surface with presorbed oxygen, hydrogen is released into the gaseous phase after adsorption of 10 . 10^{20} hydrogen sulphide molecules. The amount of the released hydrogen in further adsorption of hydrogen sulphide was very small as compared with the amount released in hydrogen sulphide adsorption on clean catalyst surface. The amount of hydrogen released into the gaseous phase was determined in a separate measurement. Up to 9·1 . 10^{20} hydrogen sulphide molecules no gas appeared in the gaseous phase. When further portion was admitted 5·6 . 10^{20} molecules of hydrogen sulphide were adsorbed. After this adsorption the gaseous phase contained 1·1 . 10^{20} hydrogen molecules and 0·1 . 10^{20} molecules of a gas, condensing in liquid nitrogen, but not in a bath of solid carbon dioxide. Since the partial pressure of this gas decreased with time, we could assume that it was hydrogen sulphide which gradually adsorbed on the catalyst.

As already noted, water is formed when hydrogen sulphide is adsorbed on presorbed oxygen. Under the given conditions water was the only reaction product. This resulted even from the mass balance of simultaneous gravimetric and volumetric analyses.

The weight of the catalyst with presorbed oxygen was

$$G(O_2) = G(R) + g(O_2),\qquad(1)$$

where $G(O_2)$ is the total weight of the catalyst, $G(R)$ is the weight of the catalyst after reduction and evacuation and $g(O_2)$ is the weight increase of the catalyst after oxygen adsorption. After adsorption of hydrogen sulphide on the surface with presorbed oxygen the weight of the catalyst was

$$G(H_2S) = G(O_2) + g(H_2S) - g(H_2O),\qquad(2)$$

where $G(H_2S)$ is the weight of the catalyst after hydrogen sulphide adsorption, $g(H_2S)$ is the weight increase of the catalyst, caused by hydrogen sulphide adsorption and $g(H_2O)$ is the weight decrease of the catalyst due to water desorption. The value of $G(H_2S)$ is obtained from the extension of the quartz helix after adsorption of hydrogen sulphide, $G(O_2)$ is known from preceding measurements. From Eq. (2) it is evident that the amount of desorbed water must be determined in order to know $G(H_2S)$. Its determination has already been described in Experimental. From the determined value of $g(H_2O)$ the value of $G(H_2S)$ could be calculated.

For this reason the amount of hydrogen sulphide adsorbed was measured both volumetrically and gravimetrically. E.g., in one of the experiments, the volumetrically

determined amount was $17.7 \cdot 10^{20}$ hydrogen sulphide molecules, and the value found gravimetrically was $18.0 \cdot 10^{20}$ molecules. This agreement confirmed the assumption that water is released from the catalyst. If the desorbed gas were *e.g.* sulphur dioxide, then the amount of hydrogen sulphide molecules adsorbed, as calculated according to Eq. (2), would be $29.4 \cdot 10^{20}$.

In this type of interaction the sorbed amount of hydrogen sulphide is higher (in the average by 50%) than that sorbed on a clean surface ($22.6 \cdot 10^{20}$ molecules were sorbed averagely on a clean surface). 50—70% of the initially sorbed oxygen were removed from the catalyst surface as water.

Adsorption of hydrogen sulphide on a catalyst with presorbed hydrogen sulphide and oxygen. This type of interaction is analogous to the preceding type. The presence of oxygen on the catalyst causes a further sorption of hydrogen sulphide. At first the rate of sorption is high, with further portions it becomes slower. Total amount of hydrogen sulphide which remained bound on the catalyst is up twice as high as the amount bound on a clean surface. The presence of oxygen on the catalyst enhances its capacity towards volume sulphidation. As in the preceding case also here water was formed by desorption from the catalyst and was then condensed in a cooled freezing trap. In this type of hydrogen sulphide adsorption about 90% of the initially sorbed oxygen was displaced in the form of water from the catalyst.

DISCUSSION

Most of the papers dealing with the adsorption of oxygen[5-7] on nickel result in the statement that one molecule of oxygen corresponds to one nickel atom at room temperature. Agreement was also attained as far as the mechanism of adsorption is concerned: it is assumed that at room temperature oxygen is adsorbed by dissociative mechanism[8,9]. As the number of sorbed oxygen atom is twice as high as the number of nickel centers, the surface adsorption proper must necessarily be accompanied by incorporation into deeper nickel layers.

When hydrogen sulphide is adsorbed on clean surface of the catalyst, approximately the same number of sulphur atoms was bound at 55°C as was the number of oxygen atoms at 20°C (see[4]). Moreover, c. 25% hydrogen from the sorbed hydrogen sulphide remained bound on the surface. It follows from the comparison of the number of sorbed hydrogen sulphide molecules with the number of active surface centers that even in this case besides surface chemisorption also incorporation of sulphur into the surface takes place, *i.e.* a partial sulphidation of the sub-surface nickel atoms occurs. Further considerations on the mechanism of interactions start with a catalyst on which an oxidized or sulphidated layer of nickel atoms is present on the surface. The extent of oxidation or sulphidation is approximately the same in both cases. Since 1 g of the catalyst contained $60 \cdot 10^{20}$ nickel atoms, it follows that after oxygen or hydrogen sulphide sorption c. one third of the nickel atoms is occupied.

In the interaction of hydrogen sulphide with presorbed oxygen the formation of water was observed. One can assume that the bound oxygen is displaced by sulphur and after reaction with hydrogen is released in the form of water. In order to compare the behaviour towards hydrogen sulphide of the presorbed oxygen with that of the oxygen in normal oxide we followed the interaction of hydrogen sulphide with nickel oxide. These experiments were carried out under the same conditions as in the interaction of hydrogen sulphide with presorbed oxygen. After admitting hydrogen sulphide on to the NiO sample water appeared in the gaseous phase. As in the case of presorbed oxygen here, too, oxygen was displaced by sulphur and reacted with the hydrogen of the hydrogen sulphide yielding water which condensed in a cooled freezing trap. E.g., when $21·3 . 10^{20}$ molecules of hydrogen sulphide were adsorbed $17·4 . 10^{20}$ molecules of water were released. Similar result was obtained by Colson[10] at high temperatures. The author presumes that hydrogen sulphide molecules diffuse into the NiO lattice below the already formed layer of sulphide, whereas water molecules diffuse towards surface. The author does not take into account the diffusion of nickel atoms.

In the first stages of the interaction of hydrogen sulphide with presorbed oxygen sulphur can more easily displace oxygen than to (up to $10 . 10^{20}$ molecules) interact with further nickel atoms below the oxide layer. As already mentioned in Results. after c. $10 . 10^{20}$ hydrogen sulphide molecules were adsorbed, hydrogen is gradually released into the gaseous phase. This finding indicates that in this case further nickel atoms, obviously below the initially oxidized layer, are sulphidated. This further sulphidation proceeds parallel to the reaction of hydrogen sulphide with presorbed oxygen and, according to the amount of hydrogen released into the gaseous phase, to a lower extent.

In the adsorption of hydrogen sulphide on a catalyst with presorbed oxygen more hydrogen sulphide molecules were sorbed than on a clean surface under otherwise identical conditions. The same result was obtained in analogous experiments with hydrogen selenide[3]. The higher amount of sorbed hydrogen sulphide is apparently the result of partial destruction of the nickel lattice by oxygen and consequently it causes a further sulphidation.

In the interaction of oxygen with presorbed hydrogen sulphide neither water nor any other gaseous component is found. In this case the results are rather difficult to interpret. Both the course of adsorption and the amount of the sorbed oxygen are the same as on a clean catalyst surface. Assuming that the number of active centers for oxygen adsorption is the same as on a clean surface, the principal problem remains, i.e. how and on which sites it is bound, whether to the sulphide in molecular or atomic form or to further nickel atoms.

Some data connected with these problems were obtained when studying the adsorption of hydrogen sulphide on a catalyst on which hydrogen sulphide ($20 . 10^{20}$ molecules) and oxygen ($10 . 10^{20}$ molecules) were adsorbed consecutively. Adsorption

of the first portions of hydrogen sulphide on this oxosulphidated surface was instantaneous. Here it must be taken in account that the catalyst was already occupied by $20 . 10^{20}$ hydrogen sulphide molecules and that the adsorption of further amounts of this substance would proceed in the absence of oxygen very slowly. The presence of oxygen enhances considerably the rate of hydrogen sulphide adsorption. If we assumed that oxygen is bound on the surface with presorbed hydrogen sulphide in molecular form, it would be rather difficult to explain why further sorption of hydrogen sulphide is accelerated by oxygen. If we assume the oxygen adsorption to proceed *via* a dissociative mechanism, then, with respect to the amount of bound oxygen atoms, further nickel atoms must take part in the interaction which are not bound to sulphur. This interpretaion has been verified by measuring the magnetic changes in the interaction oxygen–hydrogen sulphide[11]. Interaction of hydrogen sulphide (at 25°C) with presorbed oxygen did not cause any change in magnetization, whereas in the adsorption of oxygen on a catalyst with presorbed hydrogen sulphide it decreased from the beginning of the adsorption process. In this case oxygen is at least partially bound to free nickel atoms. This leads to a further destruction of the nickel lattice which is manifested in the subsequent interaction of hydrogen sulphide with this surface. When hydrogen sulphide is admitted on a catalyst which has been oxosulphidated in the described manner it displaces oxygen in the form of water and becomes bound on its site. Consequently, the thickness of the sulphide layer is increased.

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