DETERMINATION OF THE SURFACE AREA OF NICKEL IN A Ni/Al₂O₃ CATALYST USING THE METHOD OF CHEMISORPTION AND OF MAGNETIZATION CHANGES

A.RUDAJEVOVÁ and V.POUR

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

The adsorption of H_2, O_2, CO, H_2S and N_2O at room temperature was measured on a methanation catalyst Ni/Al_2O_3 with the aim to compare the suitability of the mentioned gases for the determination of nickel surface area. In order to distinguish the consecutive processes from chemisorption itself the changes of magnetic properties of the catalyst during adsorption were estimated with an A.C. permeameter. The adsorption of all the gases studied caused a decrease in magnetization. Comparison of the slopes of magnetic isotherms of the studied gases with that of the hydrogen isotherm allowed to characterize the adsorption mechanism. The values of the surface area of nickel as determined from chemisorption of hydrogen, carbon monoxide and hydrogen sulphide are very close. With oxygen, incorporation takes place, which is evidently deeper than the commonly found two-layer value.

The knowledge of the surface area of the active component in multicomponent catalysts is a necessary condition for the determination of both the mechanism and the extent of adsorption of the studied adsorbates, as well as for the determination of the specific activity of catalysts. The most commonly used method of surface area determination is based on specific chemisorption of gases on their active component. Chemisorption of hydrogen[1-5], oxygen[6-8], carbon monoxide[1,2], hydrogen sulphide[8] and thiophene[8,9] was proposed for the determination of the surface area of nickel in multicomponent catalysts. Each of these adsorbates has its pros and cons, obviously differing for various systems. So, *e.g.*, Beeck[10] who worked with nickel films, preferred carbon monoxide to hydrogen because of its solubility in nickel. Unlike him, Schuit and van Reijen[2] prefer to use hydrogen when determining the surface area of the nickel in a Ni/SiO_2 catalyst since carbon monoxide may be physically adsorbed on nickel at low temperatures and at higher temperatures may react under the formation of carbonyl.

In our previous publications[11,12] we have used oxygen for the determination of the surface area of the nickel component in the Ni/Al_2O_3 catalyst. In the study of hydrogen adsorption a great difference was found between the amounts of sorbed hydrogen and those of oxygen at room temperature and thus the problem arose which of the two gases would be suitable for the determination of the surface area of the nickel component. For this reason the present paper is devoted to the study of adsorption of H_2, O_2, CO, H_2S and N_2O. The results obtained in measuring the magnetization

changes during adsorption were also employed to choose the most suitable adsorbate for surface area measurements. These results were used both to distinguish the chemisorption itself from consecutive processes and to find the mechanism of adsorption.

Nickel in the Ni/Al_2O_3 catalyst, used in our experiments, is dispersed in such a manner that nickel particles behave as a superparamagnetic substance[14]. The change in its relative magnetization during adsorption is described by the relation[14]

$$\Delta M/M = -2n_H \Theta \beta/\mu n + \left(n_H \Theta \beta/\mu n\right)^2, \qquad (1)$$

where $\Delta M/M$ is the relative change in magnetization, n_H is the number of adsorbed atoms of hydrogen (represents the number of bonds), Θ is the change of the magnetic moment of nickel caused by adsorption of one hydrogen atom, β is Bohr's magneton, μ is the magnetic moment of nickel atom and n is the number of nickel atoms in the studied sample.

EXPERIMENTAL

Adsorption of the individual gases was measured volumetrically. Final equilibrium pressures were about 10 Torr. Pressures of the gases in the apparatus were read off by means of a cathetometer KM 6 (USSR) on a U-shaped manometer.

The catalyst Ni/Al_2O_3 was prepared by continuous precipitation of a solution of nickel(II) nitrate by sodium aluminate. After calcination and pressing into tablets under addition of graphite the catalyst was reduced by hydrogen, the final temperature being 425°C. After cooling the sample was passivated by controlled chemisorption of oxygen. Prior to measurement this catalyst was again reduced in hydrogen at 400°C for 30 hours. Evacuation was carried out at 420°C up to the pressure of the order of magnitude of $10^{-4}-10^{-5}$ Torr. In the reduced state the catalyst contained 50·2 w.% Ni. Total surface area was 160 m^2/g of the reduced catalyst.

The gases were taken from steel flasks. Electrolytic hydrogen was purified by passing over molecular sieve. The residual traces of water were removed in the apparatus by passing through freezing traps, cooled by a mixture of solid carbon dioxide and ethanol. Oxygen was fed through an ampoule with KOH and was further purified in a cooled freezing trap. The same procedure was maintained in purifying CO and N_2O. Hydrogen sulphide was passed through a cooled freezing trap and then condensed in the apparatus in a bath of liquid nitrogen. Afterwards it was purified several times by evacuation.

Changes of magnetic properties were measured with an A.C.-permeameter described in our previous paper[13].

Cleanness of the surface (especially whether all hydrogen was removed which could affect the subsequently adsorbed amount of hydrogen) was checked in a few experiments in which the time of evacuation was prolonged from the usual four to ten hours. This prolongation resulted in a decrease of the subsequently adsorbed amount of hydrogen from 2·9 to 2·6 . 10^{20} molecules/g. This is evidently caused by the decrease of the surface area by sintering.

Sintering of the nickel catalyst also takes place when reduction temperature is higher, or in repeated reduction of the same sample. The sintering was verified by magnetization measure-

ments. So, *e.g.*, if the sample of the catalyst was reduced at 500°C instead of 400°C, magnetization M (measured at room temperature) increased by 26%. Magnetization of a superparamagnetic substance obeys the relation[14]

$$M = VI_{sp}^2 vH/3kT,\qquad(2)$$

where V is the total volume of the sample, v is the volume of the particle (domain), H is the intensity of magnetic field, k is Boltzman's constant, T is temperature and I_{sp} is the spontaneous magnetization. From the relation it is evident that the increase in magnetization is caused by the increase of particle volume, since the magnetization was measured at constant temperature and at constant intensity of magnetic field.

Both the above-mentioned results show that in all experiments to be compared the same reduction and evacuation procedures should be preserved.

RESULTS

Adsorption of hydrogen. Adsorption of hydrogen was carried out portionswise $(0.2-0.5 . 10^{20}$ molecules). Total $2.9 . 10^{20}$ molecules/g reduced catalyst were adsorbed. All further data will be related to 1 g of the reduced catalyst. From the total amount adsorbed, $2.3 . 10^{20}$ molecules were adsorbed irreversibly, the remaining $0.6 . 10^{20}$ molecules were bound reversibly.

Relative magnetization (Fig. 1) decreased linearly during adsorption. The slope of magnetic isotherm was 0.032. Up to about $1.8 . 10^{20}$ hydrogen molecules adsorbed the adsorption proceeded at a high rate and was totally irreversible. After evacuation of the gaseous phase up to the mentioned amount of adsorbed hydrogen magnetization remained constant. Adsorption of a further amount of hydrogen was
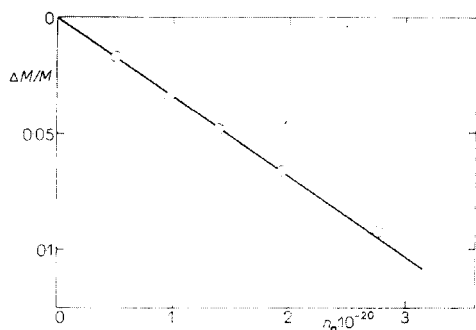

FIG. 1

Magnetic Isotherm for Hydrogen
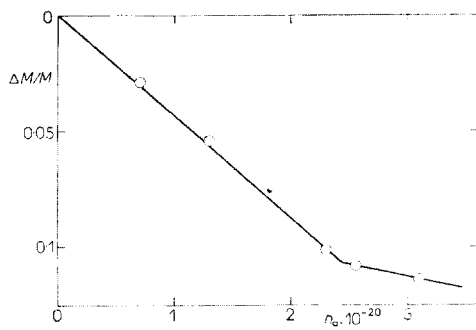n_a Adsorbed amount of hydrogen (molecules/g), $\Delta M/M$ relative magnetization.

FIG. 3

Magnetic Isotherm for Carbon Monoxide

slower than the first portion and evacuation resulted in a partial increase in magnetization. Admission of each further amount of hydrogen after evacuation led to a new decrease in magnetization.

Adsorption of oxygen. Total amount of oxygen adsorbed was (average) $8.3 \cdot 10^{20}$ molecules. All oxygen was bound irreversibly. Relative magnetization decreased linearly with the slope 0.060. Magnetic isotherm is shown in Fig. 2.

Adsorption of carbon monoxide. At room temperature carbon monoxide is adsorbed instantaneously till the state is attained when about $2.5 \cdot 10^{20}$ molecules
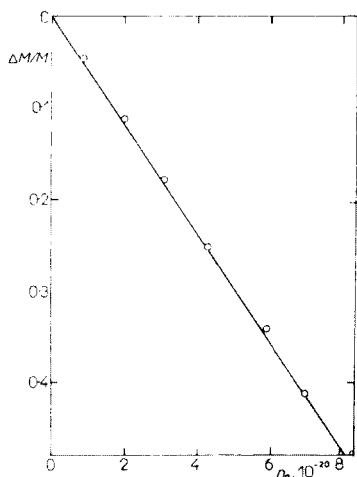

Fig. 2

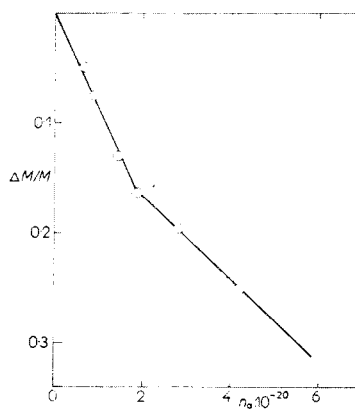Magnetic Isotherm for Oxygen
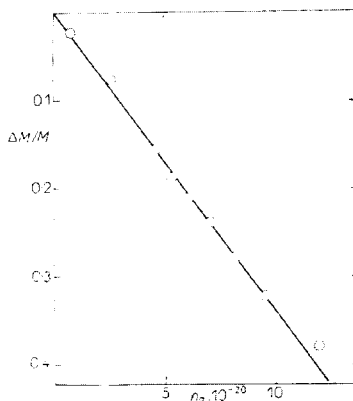

Fig. 4

Magnetic Isotherm for Hydrogen Sulphide

Fig. 5

Magnetic Isotherm for Nitrous Oxide

are present on the surface. Then the rate of adsorption decreases considerably. By means of magnetic measurements this chemisorption could be distinguished from consecutive processes. In the process of adsorption, magnetization at first decreased linearly with the slope 0·044. In the moment when approximately $2·5$ . . 10^{20} molecules are bound to the catalyst, a break occurs on the isotherm and the following part of the isotherm is almost parallel to the axis of the adsorbed amount (Fig. 3). After evacuation of the gaseous phase in the final phase of adsorption, relative magnetization increases again, attaining the value which corresponds to $2·6$. 10^{20} molecules adsorbed. Totally, $3·3$. 10^{20} molecules of carbon monoxide were adsorbed. Of this the chemisorbed portion was $2·5$. 10^{20} molecules (as determined from the intersection of both parts of the isotherm).

Adsorption of hydrogen sulphide. Detailed data on the adsorption of hydrogen sulphide as well as on the relative changes in magnetization are given in our preceding paper[13]. Magnetic isotherm is shown in Fig. 4. In adsorption on a clean surface of the catalyst adsorption proceeds completely and without any release of hydrogen into the gaseous phase, up to the moment when about $1·7$. 10^{20} molecules are adsorbed on the surface. In this first phase magnetic isotherm is represented by a straight line with the slope 0·080. In further adsorption hydrogen is released into the gaseous phase, the adsorption rate decreases significantly and the slope of the magnetic isotherm diminishes to one half of its initial value, *i.e.* to 0·42.

Adsorption of nitrous oxide. Nitrous oxide is adsorbed at room temperature *via* dissociative mechanism, wherein oxygen is bound to nickel and nitrogen is released into the gaseous phase. Consequently, the amount of nitrogen monoxide adsorbed cannot be determined by direct measurement of the pressure and it is necessary to determine the amount of nitrogen in the gaseous phase in each measurement. The pressure of the released nitrogen was measured after freezing out dinitrogen monoxide in a trap with liquid nitrogen. Total final pressure in the apparatus was c. 25 Torr. The adsorbed amount depends considerably on time, since nitrogen which remains in the gaseous phase after adsorption, reduces the adsorption rate. So, *e.g.*, $32 . 10^{20}$ molecules were adsorbed within 15 hours. Magnetization decreased, the slope of the linear isotherm being 0·03 (Fig. 5).

DISCUSSION

Hydrogen. From the results it follows that hydrogen is adsorbed on the catalyst used both reversibly and irreversibly. However, both kinds of adsorption have the same effect on the relative change in magnetization. Magnetic isotherm is a straight line. From this it can be assumed the both kinds of adsorption proceed *via* the same mechanism. If the irreversible adsorption is assumed to proceed so that one hydrogen atom is bound to one nickel atom, we must also assume that the reversible part
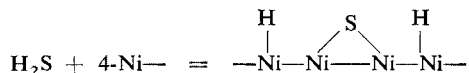
of hydrogen is bound in the same way, and thus we can exclude *e.g.* a molecular form of bonding. However, with respect to surface area determination the important question is whether the mentioned reversible hydrogen is bound to the surface nickel centers. Some authors[15], when determining the surface area by chemisorption, do not distinguish at all the character of the sorbed hydrogen, in spite of the fact that there are data and discussions in the literature on the different kinds of the sorbed hydrogen. According to Goundry and Tompkins[17], the processes taking place in adsorption are temperature dependent. At low temperatures, up to 195 K, the slow process may be explained as a surface phenomenon. At room temperature and at higher temperatures both absorption and adsorption of hydrogen take place. Suhrman[18] found a reversible portion of the bound hydrogen and considers the possibility of its dissolving in nickel. According to his interpretation hydrogen penetrates into the lattice of the catalyst in atomic form. After evacuation the atoms are recombined to form hydrogen molecules which is then desorbed from the surface. In accordance with this conception we also assume that the reversible part of hydrogen is not bound to the surface and consequently cannot be taken into account when calculating the surface atoms of nickel. Therefore only irreversible hydrogen, *i.e.* $2.3 . 10^{20}$ molecules are included in the determination of the nickel surface area. Provided that hydrogen is bound dissociatively and that each hydrogen atom occupies one surface nickel, *i.e.* the area of $6.7 \, \text{Å}^2$ (see[19]), the surface area of nickel is $31 \, \text{m}^2$.

Oxygen. The total of the adsorbed amount is bound irreversibly. Under the commonly accepted assumption that one oxygen molecule comes per one surface nickel[20,21], we can deduce that there are $8.3 . 10^{20}$ centers on the nickel surface. This would correspond to the surface area $55 \, \text{m}^2$. The slope of magnetic isotherm of oxygen is twice as great as that of hydrogen. According to Selwood's method[22], four bonds are formed per one oxygen molecule.

Carbon monoxide. From Fig. 3 it can be seen that the isotherm of carbon monoxide consists of two parts. The average value of the adsorbed amount at the point of the break on the isotherm was $2.5 . 10^{20}$ molecules. As already stated in the results, after evacuation of the gaseous phase at the end of the isotherm the relative magnetization increased. The value of the adsorbed amount at which the magnetization does not change by evacuation, was $2.6 . 10^{20}$ molecules. This means that the whole second part of the isotherm corresponded to reversible adsorption. Den Bensten and Selwood[23] also found the magnetic isotherm to consist of two parts. Their interpretation is as follows: The first part of the isotherm corresponds to adsorption *via* a linear mechanism the second one to the formation of bridge bonds, but on nickel atoms, to which the molecules of carbon monoxide have already been bound by linear. mechanism. The same interpretation of the found IR bands is presented by Yates and Garland[24]. If we applied this explanation to the second part of the isotherm

as found in our experiments, then the molecules bound in this way would anyhow be not included into the calculation of the nickel surface area. For this reason the value $2 \cdot 5 . 10^{20}$ molecules was chosen for determining the surface area of nickel. This value corresponds to the linear decrease of magnetization with the slope $0 \cdot 044$. This slope is $1 \cdot 3$ times greater than that of the magnetic isotherm of hydrogen. Consequently we assume that one molecule of carbon monoxide is bound to the surface by two bonds so that one molecule blocks two nickel centers. Accordingly, the surface area of nickel is 33 m^2.

Hydrogen sulphide. As can be seen from Fig. 4, magnetic isotherm of hydrogen sulphide consists of two linear parts. The slope of the first part is twice as great as the slope of the second one which has the same value as for hydrogen. Using the already mentioned comparison method for the determination of the number of bonds, the following mechanism was proposed of the adsorption of hydrogen sulphide on a clean surface of the catalyst

$$
\mathrm{H_2S} + 4\text{-Ni}\!-\!- \;\rightleftharpoons\; \begin{array}{ccc} \mathrm{H} & \mathrm{S} & \mathrm{H} \\ | & \diagup\!\diagdown & | \\ -\!\mathrm{Ni}\!-\!\mathrm{Ni}\!-\!\!-\!\mathrm{Ni}\!-\!\mathrm{Ni}\!- \end{array}
$$

After total coverage of the surface the bonding of hydrogen sulphide begins, accompanied by the release of one hydrogen molecule into the gaseous phase and the bonds —Ni—S—Ni— are formed under the surface. A volume sulphidation sets in. Under the assumption that surface adsorption can be distinguished from volume sulphidation, hydrogen sulphide can be used for the determination of nickel surface area. The value, decisive for the surface area determination is the amount of sorbed hydrogen sulphide in the break point on the magnetic isotherm. This break occurs at $1 \cdot 7 . 10^{20}$ molecules adsorbed. Since in this phase one molecule is bound to the surface by four bonds, the number of centers determined in this manner is $6 \cdot 8 . 10^{20}$.

In addition to this, reversible adsorption of hydrogen takes place on a catalyst whose surface was saturated with hydrogen sulphide. In the interaction of hydrogen sulphide with the catalyst the surface adsorption is followed by volume sulphidation, in which hydrogen is released into the gaseous phase. This hydrogen is bound to sites, accessible to reversible hydrogen adsorption and thus it affects the magnetization in the same way as irreversible hydrogen. Therefore the first part of the isotherm will include the portion of volume sulphidation with reversible hydrogen adsorption. However, this portion is not characteristic for surface area determinations. Similarly as in the case of surface area determination by means of hydrogen adsorption, also here a correction was made for reversibly bound hydrogen. After this correction the number of surface centers of nickel is $5 \cdot 6 . 10^{20}$ and the corresponding surface area is 37 m^2.

Nitrous oxide. As commonly accepted, adsorption of nitrous oxide on a nickel catalyst proceeds *via* a dissociative mechanism, *i.e.*, oxygen is bound to nickel and nitrogen is released into the gaseous phase. According to this conception the adsorption of nitrous oxide was expected to stop, as soon as the amount of oxygen bound to the catalyst amounts the coverage in one or two monolayers, as it is in the case of oxygen adsorption. However, the results have shown that oxygen from the nitrous oxide molecule is sorbed even further, up to the amount corresponding to more than two monolayers. The amount of oxygen adsorbed in this way depends then on the time of the experiment, since even when $32 . 10^{20}$ oxygen atoms are sorbed the adsorption does not cease. No adsorption was observed to take place of nitrous oxide on a Al_2O_3. On the basis of these results nitrous oxide does not seem to be suitable for the determination of nickel surface area. Magnetic measurements confirm the above assumed adsorption mechanism. The slope of the linear magnetic isotherm is only one half of the value of the slope of oxygen which proves that one oxygen atom is bound from the nitrous oxide molecule.

The final task is to decide which of the studied gases is the most suitable one for the determination of surface area of nickel in the Ni/Al_2O_3 catalyst. Nitrous oxide can unambiguously be excluded, since here a deep oxidation of nickel takes place and neither the magnetic method allows to distinguish the surface adsorption from oxidation. Table I presents a review of surface areas of nickel as determined by chemisorption of the studied gases together with the suggested adsorption mechanism. From the Table it is evident that oxygen yields a considerably higher value of surface

TABLE I

Surface Areas of Nickel

Gas	Surface area m^2/g	Mechanism of chemisorption
H_2	31	H H | | —Ni—Ni—
O_2	55	O O ∥ ∥ —Ni—Ni—
CO	33	O ∥ C / \ —Ni——Ni—
H_2S	37	H S H | / \ | —Ni—Ni——Ni—Ni—

area than other gases, which is obviously the result of the deeper incorporation than to the usually reported two monolayers. The main drawback of H_2, CO and H_2S for the determination of surface area are the processes which follow the chemisorption. However, magnetic measurements made it possible to distinguish the chemisorption itself from these consecutive processes. The average value of the surface area of nickel, determined by means of hydrogen, carbon monoxide and hydrogen sulphide adsorption, was 34 m^2.

REFERENCES

1. Brooks S. C., Christopher L. G. M.: J. Catal. *10*, 211 (1968).
2. Schuit G. C., van Reijen L. L.: Advan. Catal. *5*, 243 (1958).
3. Sinfelt J. H., Taylor W. F., Yates D. C. J.: J. Phys. Chem. *65*, 95 (1965).
4. Mars P., Scholten J. J. F., Zwietering P.: *Actes du Deuxiéme Congress International de Catalyse, Paris 1960*, p. 1245. Technip, Paris 1961.
5. Taylor W. F., Sinfelt J. H., Yates D. C. J.: J. Phys. Chem. *69*, 3857 (1965).
6. Emmet P. H., Brunauer S.: J. Am. Chem. Soc. *59*, 1553 (1937).
7. Vlasenko V. M., Rusov M. T., Juzefovič G. E.: Kinet. Katal. *2*, 409 (1962).
8. Ljubarskij G. D., Avdejeva L. B.: Kinet. Katal. *4*, 409 (1963).
9. Ljubarskij G. D., Avdejeva L. B., Kulkova N. V.: Kinet. Katal. *2*, 123 (1962).
10. Beeck O.: Advan. Catal. *2*, 151 (1950).
11. Rudajevová A., Pour V., Regner A.: This Journal *38*, 2566 (1973).
12. Rudajevová A., Pour V.: This Journal *39*, 2130 (1974).
13. Rudajevová A., Pour V.: This Journal *39*, 3048 (1974).
14. Selwood P. W.: *Actes du Deuxiéme Congress International de Catalyse, Paris 1960*, p. 1795. Technip, Paris 1961.
15. Bousqet J. L., Techner S. J.: Bull. Soc. Chim. France *10*, 3687 (1972).
16. Bröcker F. J., Wedler G.: Discussions Faraday Soc. *41*, 87 (1966).
17. Goundry P. M., Tompkins F. C.: Trans. Faraday Soc. *53*, 218 (1957).
18. Suhrman R.: Advan. Catal. *7*, 303 (1955).
19. Max Rae A.U.: Surface Sci. *1*, 319 (1964).
20. Delchar T., Tompkins F. C.: Surface Sci. *8*, 165 (1960).
21. Müller J.: *Thesis.* Institute of Chemical Technology, Prague 1960.
22. Selwood P. W.: *Adsorption and Collective Paramagnetism*, p. 130. Academic Press, New York, London 1962.
23. Den Bensten I. E., Fox P. G., Selwood P. W.: J. Phys. Chem. *86*, 450 (1962).
24. Yates J. T., Garland C. W.: J. Phys. Chem. *6*, 617 (1961).

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