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A Study of the Oxygen Adsorption on Nickel

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Oxygen adsorption on nickel was studied in connection with the more general problem of determination of the number of surface metal atoms (the surface area) in multicomponent catalysts by the selective chemisorption method.

Studies of the oxygen adsorption on samples of nickel powder at temperatures of 22–78°C and −196°C demonstrated that the amount adsorbed at 22°C and −78°C slowly and steadily increases with time. This phenomenon is explained by the oxygen incoporation into the crystal lattice of nickel. The processes connected with this incorporation become unmeasurably slow only at temperatures approaching that of the boiling point of nitrogen. At −78°C no physical adsorption of oxygen occurs on nickel, whereas at −196°C the major part of adsorbed oxygen is bound by physical adsorption. It was found during investigations on the thermal regeneration of the nickel surface coated by oxygen that this process does not occur to a greater extent up to temperatures exceeding 200°C, as it is quoted in the literature, but it was also found that at lower temperatures, and even at −78°C a certain part of the covered surface is regenerated in the vacuum.

On the basis of the results obtained the choice of experimental conditions which are convenient for the determination of the nickel surface area in nickel catalysts by the selective oxygen adsorption on nickel is discussed.

INTRODUCTION

An analysis of the present state of the selective chemisorption method for the determination of the metal surface area in multicomponent catalysts shows (*1*) that with respect to the dependence of the adsorptive properties on the structure of the adsorbent this method is only of conventional character. Its applicability to a given type of catalyst must therefore be considered separately for each case. In connection with the endeavor to develop a method for the determination of the nickel surface area in Ni-Cr_2O_3 catalysts [these catalysts were developed in our laboratory for the removal of oxygen, carbon monoxide, and carbon dioxide from hydrogen and hydrogen-containing gases by selective hydrogenation of oxygenous impurities to methane and/or water (*2*)], after preliminary experiments with the adsorption of various adsorbates on both components of the catalyst, oxygen adsorption on nickel was investigated in detail. The samples of nickel powder were prepared in the same way as the Ni component of the Ni-Cr_2O_3 catalyst mentioned above.

Oxygen adsorption on nickel has been studied by several authors on evaporated films (*3–8*), powders (*6, 9, 13, 14*), metal (*10*), nickel monocrystals (*11*), and on nickel catalysts (*12–15*). Some questions, however, especially those interesting us in connection with the selective chemisorption method, are not clear yet. These are the problems connected with slow processes, most often denoted as oxygen incorporation into the nickel crystal lattice.

As we assume that during direct admission of oxygen to the sample the diffusion rate of oxygen to the surface is most probably measured in the first stage, and that such an adsorption, moreover, can proceed nonisothermally [cf. (*6*)], the procedure of slow admission of oxygen to the sample was used and the kinetics of the slow adsorption stage were studied. We were interested in the character of oxygen adsorption at different temperatures and in the question whether slow processes proceed also at lower temperatures, or whether they could be frozen, as indicated by Scheuble (*4*).

EXPERIMENTAL

Materials. Oxygen adsorption was studied on two samples of nickel powder (A, B), prepared by reduction of NiO with hydrogen. The details of sample preparation can be found in a former publication (*16*). The surface area of the samples was determined by means of nitrogen (0.01% O_2), with oxygen removed in an alkaline solution of sodium anthraquinone-β-sulfonate. The nitrogen freed from oxygen in this manner was dried with H_2SO_4 and solid KOH. For the adsorption measurements oxygen (0.1% N_2 and <0.1% CO_2) was used, from which carbon dioxide was removed in a bubble flask with potassium hydroxide solution. The gas was dried afterwards with solid KOH.

Apparatus and procedure. NiO reduction was carried out in a flow apparatus by hydrogen (0.4% N_2 and <0.1% O_2), purified of oxygen on a Ni-Cr_2O_3 catalyst (*2*). Reduction proceeded at slowly increasing temperatures up to 300°C, for a total period of 8–10 hr. Surface area determination and the investigation of oxygen adsorption was carried out in a temperature-controlled apparatus, described in our previous paper (*16*).

The surface area of the samples was determined by the BET method from the adsorption isotherms of nitrogen in a pressure range of 50–150 torr (the initial pressure values moved about 80 torr) using the values of $\sigma_{N2} = 16.2$ Å^2. Surface areas of the samples were determined before oxygen adsorption, as it was found that covering of the nickel surface with oxygen leads to an increase of the V_m values of nitrogen [problems of the influence of preadsorption on the surface area determination were discussed in detail elsewhere (*16*)]. Oxygen adsorption was studied at temperatures of 22°, $-78°$, and $-196°$C, in a pressure range of 10–100 torr, following the pressure changes at constant volume. In this pressure range the adsorbed amount of oxygen does not depend on the pressure anymore, the stationary oxygen pressure is stated to be much lower, 10^{-3} torr (*3*) and 10^{-6} torr (*5*). Degassing of the reduced samples was considered complete when a pressure of 1.10^{-5} torr at a sample temperature of 300°C was attained in the apparatus. The adsorbed nitrogen can be removed from the nickel surface by 1 hr evacuation at $-78°$C; evacuation was again finished at a pressure of 1.10^{-5} torr.

RESULTS AND DISCUSSION

Adsorption at 22°C

The results of measurements on Sample A3 are summarized in Table 1. The table shows that the amount of oxygen adsorbed on the reduced sample as well as that found after the evacuations following adsorption, slowly and steadily increase with time. This fact is considered to be caused by oxygen incorporation into the nickel crystal lattice. Incorporation generally has the consequence that on the oxygen-covered surface free nickel atoms appear, adsorbing further oxygen portions from the gas phase. Several mechanisms have been proposed for oxygen incorporation (*3, 4, 5, 17, 18*):

(1) Migration of oxygen ions (probably O^-) into the crystal lattice of nickel.

(2) Migration of nickel atoms or ions to the surface covered with oxygen.

(3) Recrystallization of the surface layer followed by appearance of free nickel atoms.

It follows from Table 1 that the adsorbed amount (measured after the same interval of 30 min) also increases with rising temperature of the previous evacuation. This fact could be caused either by oxygen desorption increasing with rising evacuation temperature, or by oxygen incorporation into the crystal lattice. Incorporation occurring during evacuation of the sample (i.e., in absence of oxygen in the gas phase) is denoted (*17, 18*) as thermal regeneration of the nickel surface covered with oxygen. Evacuation at 165°C and 315°C was carried out in such a way that the vessel containing the sample was connected during the heating

TABLE 1

OXYGEN ADSORPTION ON NICKEL AT 22°C[a]

Pretreatment	Time (min)	V_{ads} (NTP ml O_2)	V_{ads} total (NTP ml O_2)	$\Theta^b = O/Ni$
Reduction	92	4.54	4.54	2.08
	100	4.67	4.67	2.14
1-hr evacuation at 22°C	30	0.34	5.01	2.29
	60	0.46	5.13	2.35
	After further 14.5 hr	1.01	5.68	2.60
1-hr evacuation at 165°C	30	0.43	6.11	2.79
1-hr evacuation at 315°C	30	1.16	7.27	3.33
	160	2.09	8.20	3.75
	After further 90 hr	2.49	8.60	3.94

[a] Sample A3, $W = 1.7$ g, $S_w = 7.87$ m^2.

[b] Surface coverage is expressed as the number of oxygen atoms corresponding to one surface atom of nickel. A uniform distribution of crystal faces (111), (100), and (110) on the nickel surface is assumed, the area corresponding to one nickel atom on the crystal face (111) amounts to 5.3 Å², on that of (100) 6.15 Å² and on face (110) 8.7 Å².

with the evacuated part of the apparatus where pressure measurements were carried out. As oxygen desorption was not observed at 315°C either it is clear that thermal regeneration of the surface occurs during evacuation. The extent of this regeneration increases with rising temperature of evacuation. To be able to express the extent of thermal regeneration quantitatively, the time dependence of the adsorbed amount of oxygen after evacuation at 22°C (given by incorporation) was replaced by a straight line in a range from 0 to 60 min and thus the extrapolated adsorption value for zero time was found. This value represents the extent of thermal regeneration after 1 hr evacuation at 22°C. The following actual values could be derived from Table 1:

0.12 NTP ml O_2 (0.46–0.34), for the incorporation value at 22°C in the course of 30 min;

0.22 NTP ml O_2 (0.34–0.12) = 0.0295 ml/m², for the adsorption value at zero time (after 1 hr evacuation at 22°C).

The second of both values mentioned above represents the extent of thermal regeneration after 1 hr evacuation at 22°C and after conversion for the surface coverage this value amounts to 10% of Θ_m (Θ_m is the surface coverage corresponding to a monolayer, assuming that there is one atom of oxygen for one surface nickel atom). For the temperatures of 165°C and 315°C the values of 14% and 48% Θ_m, respectively, were found in the same way. It must be considered that the thermal regeneration values expressed with respect to the original adsorption capacity of the sample attain only one-half of the values expressed as the surface coverage, as the adsorption extent in the first stage amounted to 2.075 Θ_m.

Adsorption at −78°C

In the further stage of work the question arose whether oxygen incorporation also proceeds at lower temperatures. The result of one of the measurements is presented in Fig. 1. It follows from it that slow incorporation proceeds at −78°C too, i.e., that the adsorbed amount of oxygen is time-dependent at this temperature too. The measurement was continued in the following manner: Approximatively 190 min after beginning of the measurement the sample was warmed up to 22°C by removal of the adsorption vessel from the cooling bath. The adsorption heat set free helps the equilibration of sample temperature with that of the surroundings, so that this temperature is attained in about 5 min. Figure 1 shows that by heating of the sample to 22°C incorporation gains speed and its extent increases.

By studying the character of oxygen adsorption on nickel at −78°C the results

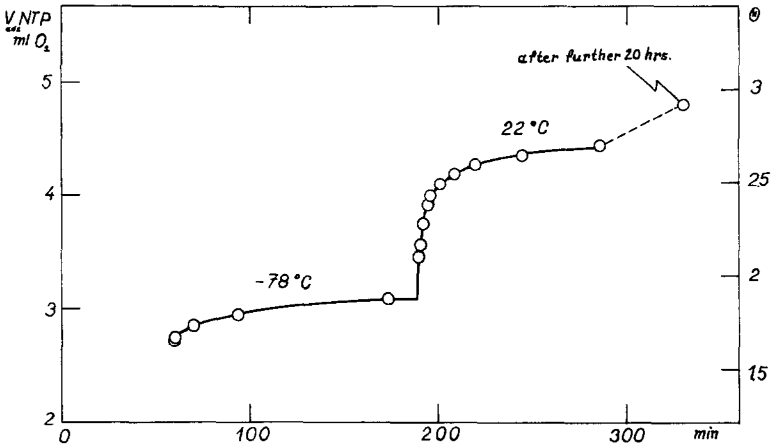

FIG. 1. Adsorbed amount of oxygen on nickel as a function of the time. Sample B1, $W = 1.061$ g, $S_w = 5.94$ m².

TABLE 2

Oxygen Adsorption on Nickel at −78°C[a]

Pretreatment	Time (min)	V_{ads} (NTP ml O_2)	V_{ads} total (NTP ml O_2)	$\Theta = O/Ni$
Reduction	113	3.69	3.69	1.95
	123	3.74	3.74	1.98
	165	3.83	3.83	2.03
1 hr evacuation at −78°C	30	0.12	3.95	2.09
	60	0.16	3.99	2.11

[a] Sample B2, $W = 1.113$ g, $S_w = 6.81$ m².

listed in Table 2 were found. The adsorption value 30 min after evacuation is ascribed again to incorporation during the period of 30 min and to the thermal regeneration of the surface caused by evacuation. By the same procedure as previously used the extent of thermal regeneration attained after 1 hr evacuation at −78°C is expressed by the value of 4% Θ_m. The plausibility of this interpretation of adsorption at −78°C, meaning that the physically adsorbed portion of oxygen is neglected, is confirmed by data obtained by adsorption studies at −196°C.

Adsorption at −196°C

In adsorption studies at this temperature emphasis was again laid on the question whether there are any slow consecutive processes and what is the character of oxygen adsorption on nickel at −196°C. The data found in the literature about the course of slow processes at low temperatures differ to a certain extent. Scheuble (*4*) states that at −190°C the slow processes accompanying oxygen adsorption are frozen; according to Oda (*5*), however, incorporation continues down to −183°C; both authors worked with evaporated nickel films. In our measurements oxygen pressure, after introduction of the gas on the sample, did not change even after a 2-hr interval. Thus it follows that at −196°C incorporation is already immeasurably slow. This result is in agreement also with the data of Quinn and Roberts (*8*), who measured changes in work function of the electron during oxygen interaction with nickel films. It follows therefore from our measurements as well as those of the authors (*4*, *8*) that it is correct to speak about a stationary state in the system nickel-oxygen only at temperatures approaching that of the boiling point of nitrogen, where the slow processes connected with incorporation are frozen.

TABLE 3

Oxygen Adsorption on Nickel at −196°C[a]

Pretreatment	V_{ads} (NTP ml O_2)	The adsorbed amount includes—
Reduction	2.805	V_{phys} (2.475 ml = 1.15 V_m) + V_{chem} (0.33 ml = 0.16 V_m)
1 hr evacuation at −196°C	2.38	Main part of V_{phys}
1 hr evacuation at −78°C	2.60	V_{phys} (2.475 ml) + $V_{th\ reg\ -78°C}$ (0.125 ml = 6% V_m)
1 hr evacuation at 22°C	2.70	V_{phys} (2.475 ml) + $V_{th\ reg\ 22°C}$ (10% V_m)

[a] Sample A4, W = 1.66 g, S_w = 7.63 m²; P_{final} = 40 torr.

The results of a study on the character of oxygen adsorption at −196°C are listed in Table 3. The presented adsorption values represent stationary values and do not change with time. Similar results on oxygen adsorption on nickel at −196°C were also obtained by Zettlemoyer *et al.* (*9*); the increase of the adsorption value at the same temperature of −196°C in dependence on the temperature of the previous evacuation is, however, explained only by the different binding strength of the oxygen portions. We assume that the physically adsorbed portion of oxygen can be removed by evacuation at −78°C [in agreement with the general convention—see, e.g., ref. (*19*)] and we believe that the increasing adsorption value after evacuation at −78°C and at 22°C is due to thermal regeneration of the surface.

The values of physically adsorbed (V_{phys}) and chemisorbed (V_{chem}) oxygen and the amount of oxygen corresponding to the thermal regeneration of the surface after 1 hr evacuation at −78°C ($V_{th\ reg\ -78°C}$) listed in Table 3 were calculated using the value $V_{th\ reg\ 22°C}$ = 10% V_m* (= 0.0295 ml/m²). The good agreement (with respect to the reproducibility of preparation of the adsorbent surface) of the value of thermal regeneration at −78°C determined from measurements carried out at −78°C (4% Θ_m) with that established from measurements at −196°C (6% Θ_m) shows that the conception of the function of thermal regeneration at 22° and −78°C is correct and the proposed interpretation consistent.

From Table 3 the interesting finding follows too, that at −196°C the chemisorbed oxygen (i.e., oxygen which was not removed from the surface by 1 hr evacuation at −78°C) covers only a smaller part of the nickel surface (in Sample A4 this part amounted to 16% Θ_m). This fact, contradictory to the hitherto usual conception that oxygen is chemisorbed on nickel in the range of one monolayer (*9*) at least, even at low temperatures, is consistent with the ideas of Davydova and Kiperman (*20*). This problem is treated in a separate paper (*21*).

Thermal Regeneration of the Nickel Surface Covered with Oxygen

Figure 2 presents a summary of data about the extent of thermal regeneration after 1 hr evacuation at different temperatures. It follows from this figure that a thermal regeneration of greater extent is attained but over temperatures of 165° to 315°C. This is in good agreement with data from the literature (*17*, *18*), where thermal regeneration of the oxygen-covered nickel surface is assumed usually only at temperature above 200°C. Our results, however, also demonstrate that thermal regeneration occurs at lower temperatures too and that the process does not stop until down to temperatures near the boiling point of nitrogen. Interpreting the adsorption data for oxygen on nickel it is therefore necessary to consider also the low-temperature regeneration of nickel surface. The thermal regeneration of the nickel surface covered with oxygen was observed at room temperatures also by Beeck *et al.* (*3*).

Discussion of Results with Respect to the Application of Oxygen for the Nickel Surface Area Determination

The data about oxygen adsorption obtained with our samples of nickel powder

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* V_m denotes the adsorbed amount of oxygen, corresponding to Θ_m.

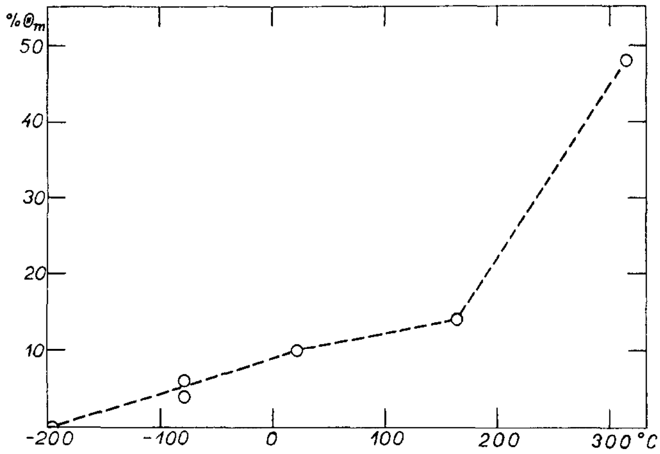

FIG. 2. The extent of thermal regeneration of oxygen-covered nickel surface after 1 hr evacuation at different temperatures.

and the set of data about the behavior of the nickel-oxygen system hitherto obtained allow for some conclusions about the choice of conditions convenient for the application of the selective chemisorption method.

Concerning the choice of the adsorption temperature the temperature of −196°C would be most favorable, from the point of view of the possibility of freezing incorporation. It cannot, however, be recommended with respect to the considerable amount of physically adsorbed oxygen on nickel as well as on the further component (in our case the structural promoter Cr_2O_3). The temperature of −78°C, used by the authors (*22*), is not favorable either as at this temperature incorporation proceeds with a measurable rate and a certain amount of physical adsorption on the other component cannot be excluded, as was found on a Ni/Al_2O_3 catalyst by Boreskov and Gorbunov (*15*). Higher than room temperatures cannot be recommended, having in view the growing extent of incorporation. From our measurements it seems most convenient to use temperatures approaching room temperatures where the extent of adsorption depends only insignificantly on the introduction rate of oxygen to the sample and amounts to about two oxygen atoms to one surface atom of nickel. The value of 2 Θ_m for the adsorption extent of oxygen on nickel at room temperatures is presented also by Brennan *et al.* (*7*) and Ljubarskij *et al.* (*13, 14*).

The pressure range of 10–100 torr used for the experiments was chosen with respect to the possibility of using a standard apparatus for surface area determinations by nitrogen. The adsorption data found in this range of pressures are in agreement with the papers (*4–9, 13, 14*), where much lower pressures were used, so that lower pressures, according to our view, do not present any special advantage. From the adsorption data of oxygen on nickel hitherto known it also follows that no difference was found between the adsorptive properties of evaporated nickel films and carefully prepared nickel powders.

Concerning the choice of the method for the determination of the adsorbed amount of oxygen, according to the results obtained it cannot be reasonably recommended to measure adsorption isotherms. The data from Table 1 and Fig. 1. proved that incorporation does not stop even after a prolonged interval. Adsorption isotherms of oxygen on nickel could have some real significance only at temperatures approaching that of the boiling point of nitrogen, when consecutive processes are already immeasurably slow and when the amount of physically adsorbed oxygen grows with increasing pressure. At higher temperatures unreal isotherms are found, where the pressure dependence measured is in fact a dependence on time. We assume that this remark applies to the papers (*3*, *12*) as well as to the method proposed for the determination of the silver area in silver catalysts (*23*). The elaboration of a conventional method for the determination of the number of nickel surface atoms in nickel catalysts, represented according to our experience by the determination of the adsorption value of oxygen at 22°C, a pressure range of 10–100 torr and controlled admission of oxygen to the sample (for a 0.5 hr duration), forms the subject of further studies in this laboratory.

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