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Adsorption Species of Oxygen on the Surfaces of Transition Metal Oxides

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A method for the determination of the mean number of elementary electric charges acquired by one oxygen atom adsorbed on the surface of such oxides as NiO, CoO, MnO is proposed. It consists of the determination of the volume of oxygen gas adsorbed on a high surface area sample of strictly stoichiometric oxide and the subsequent analytical determination of the number of metal ions promoted to a higher oxidation state as the result of electron transfer from the adsorbent to the adsorbate. Using this method it has been shown that, in the case of high surface area nickel oxide, oxygen is chemisorbed at room temperature predominantly in the form of O^- ions (irreversible adsorption). The percentage of reversibly adsorbed oxygen decreases with the time of contact. At 150°C only the O^- form was observed after a short period of adsorption. Slow formation of O^{2-} could be subsequently observed. The velocity of this latter process increases with an increase in temperature. In the case of high surface area cobalt oxide, the O^{2-} form predominates even at room temperature.

INTRODUCTION

The forms in which chemisorbed oxygen is present on the surface of transition metal oxides have been discussed in a great many papers. Simultaneous investigations on adsorption of oxygen and the changes in the electrical conductivity of such oxides as NiO (*1–3*) and Cu_2O (*4*) show that, at room temperature, chemisorption of oxygen occurs partly in the electrically neutral form and partly in the form of negatively charged species. The electrically neutral form may easily be desorbed *in vacuo*. This kind of reversible adsorption, also called molecular chemisorption, has been studied among others by Kuchynka and Klier (*1*) and Teichner and their collaborators (*2*). Conclusions concerning the nature of negatively charged adsorbed oxygen species have been formulated on the basis of investigations of adsorption heat (*3, 5, 6*), isotopic exchange of chemisorbed oxygen (*7, 8*), measurements of work function (*9, 10*), electron spin resonance (*11, 12*), kinetics of chemisorption of oxygen (*13, 14*), etc. Depending on the system investigated and the experimental conditions, the formation of O_2^-, O^- or O^{2-} ions has been postulated. The formation of O^{2-} ions is generally considered as the incorporation of chemisorbed oxygen into the crystal lattice of the oxide.

Generally the above-mentioned methods do not enable an unequivocal determination of the electrical charge associated with chemisorbed oxygen species to be made and often the same experimental results may receive different interpretations depending on the preliminary assumptions on the forms of chemisorbed oxygen.

The aim of the present investigation was to attempt to determine, in a more direct way, the number of negative charges acquired by chemisorbed oxygen molecules or atoms. In order to explain the principle of the method which we propose for this purpose, it is necessary to remember that the formation of charged chemisorbed oxygen species is accompanied by the promotion of an appropriate number of cations in the oxide crystal lattice to a higher oxidation state. In the case of NiO or CoO, this will be the oxidation of Ni^{2+} or Co^{2+} to Ni^{3+} or Co^{3+}, respectively, which, from the point of view of the semiconducting properties of the oxides, is equivalent to the formation of positive holes ($h^{\bullet}$). The following equations describe the formation of particular forms of chemisorbed oxygen:

$$O_{2(g)} \rightarrow O_{2(ads)},$$
$$O_{2(g)} \rightarrow O_2^-{}_{(ads)} + h^{\bullet},$$
$$O_{2(g)} \rightarrow 2\,O^-{}_{(ads)} + 2\,h^{\bullet},$$
$$O_{2(g)} \rightarrow 2\,O^{2-}{}_{(ads)} + 4\,h^{\bullet}.$$

They show that molecular chemisorption of oxygen is not accompanied by any electron transfer. Adsorption of oxygen in the form of O_2^- ions is connected with the formation of one Ni^{3+} (or Co^{3+} etc.) ion for one chemisorbed O_2 molecule. Adsorption of oxygen in the form of O^- ion is accompanied by the formation of 2 Ni^{3+} ions and in the form of O^{2-} by the formation of 4 Ni^{3+} ions for one chemisorbed O_2 molecule.

In the course of the experiments now reported we therefore determined the amount of oxygen adsorbed on the surface of an oxide showing stoichiometric composition and subsequently analytically determined the number of cations oxidized during chemisorption. The Bunsen-Rupp iodometric method was applied for this purpose. The whole analysis was of course carried out in an oxygen-free atmosphere without exposing the sample to the air. In several experiments the analysis was also carried out using the hydrazine method described by Uchijima (*15*).

EXPERIMENTAL METHODS

The apparatus used in the present research is schematically shown in Fig. 1. High surface area nickel oxide (NiO) and cobalt oxide (CoO) used as adsorbents in the present research were obtained by thermal decomposition of nickel hydroxide (preliminary heating at 100° for 4 hr and then for 14 hr at 200°C) or of basic cobalt carbonate (4 hr at 100° and 14 hr at 250°C) in the continuously evacuated reaction vessel 1 (final pressure 10^{-5}–10^{-6} Torr). The reaction vessel was protected from contamination by the vapors of the vacuum grease by the liquid air trap T_1. According to the experiments carried out in this laboratory by Dr. K. Dyrek, NiO and CoO obtained in the conditions described do not contain ferromagnetic impurities. On dissolving the samples in hydrochloric acid, no evolution of hydrogen took place (see Appendix) which was another indication that the samples were free from metallic nickel. No excess oxygen could be detected in such preparations and their composition was considered to be strictly stoichiometric. Their specific surface area was of the order of 100 m^2/g. The initial $Ni(OH)_2$ preparation was obtained using the method described by Merlin and Teichner (*16*), and the basic cobalt carbonate by precipitating it with $(NH_4)_2CO_3$ from $Co(NO_3)_2$ solution.

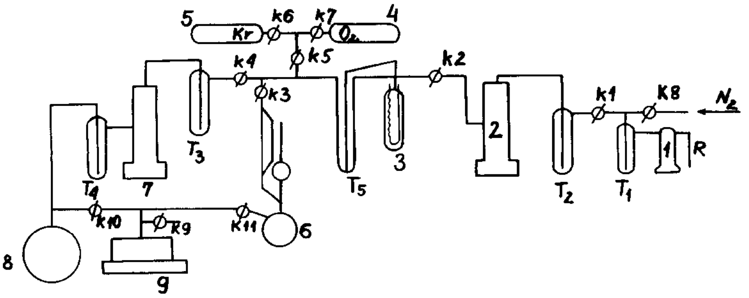

FIG. 1. Schematic diagram of adsorption system: (1) reaction vessel; (2) mercury diffusion pump; (3) Pirani gauge; (4,5) bulbs for storing O_2 and Kr; (6) McLeod gauge; (7) oil diffusion pump; (8) oil trap; (9) rotary oil vacuum pump; (T_1, T_2, T_3, T_4, T_5) liquid nitrogen traps; (k_{1-11}) vacuum taps.

The oxygen gas used for chemisorption experiments was obtained by decomposition of $KMnO_4$. It was stored in bulb 4. After evacuating the whole system by means of oil diffusion pump 7, oxygen was introduced into the known volume between taps K_1, K_3, K_4, and K_5. The mercury diffusion pump 2, which was not heated at this stage, was included in this volume. By opening tap K_1, oxygen was introduced into reaction vessel 1, and the course of chemisorption was followed by measuring the pressure changes with Pirani gauge 3 connected with a Wheatstone bridge circuit, the out-of-balance potential of which was recorded on a potentiometric recorder.

In most of the experiments, the initial pressure of oxygen was 2.7×10^{-2} Torr. After complete adsorption of the first portion of oxygen in some experiments, one or two additional equal portions of oxygen were introduced into the system. The coverage of our samples with chemisorbed oxygen never exceeded 0.6% of a monolayer. In some experiments controlled desorption of oxygen was carried out. In such cases, oxygen was pumped out from reaction vessel 1, using mercury diffusion pump 2, into the calibrated volume between the diffusion pump and K_3, K_4 and K_5 including the Pirani gauge 3. Knowing the amount of oxygen removed from the sample, the amount of oxygen irreversibly adsorbed could be calculated.

After adsorption of oxygen or adsorption and desorption of reversibly adsorbed oxygen, iodometric determination of the amount of Ni^{3+} or Co^{3+} ions in the oxide samples was made. The reaction vessel was quickly cooled to room temperature by removing the furnace, and the apparatus was filled with nitrogen thoroughly purified from traces of oxygen, using the BTS catalyst produced by the Badische Soda und Anilin Fabrik. Then the end of the side tube R of the reaction vessel was immersed in a hydrochloric acid 1:1 solution; and the tip K of tube R (Fig. 2a) was broken with pincers. By decreasing the pressure of nitrogen in the apparatus, we sucked about 10 ml of solution into vessel 1 and then again increased the pressure of nitrogen to 1 atm. Then the acid was removed from the side tube R, the end of which was immersed in a solution of KI, and the liquid in vessel 1 was heated with a small gas flame to the boiling point. The chlorine, which was evolved in the reaction

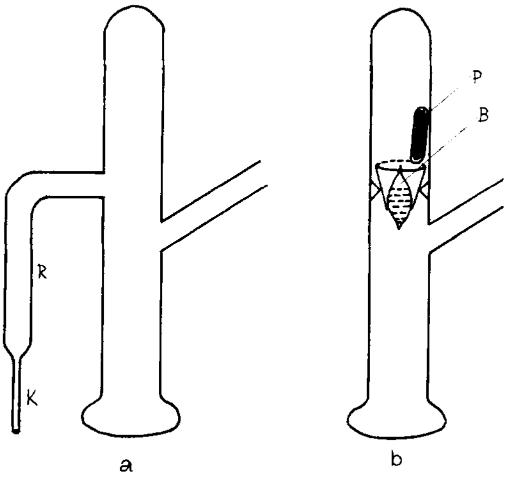

FIG. 2. Reaction vessels: (a) for the experiments with adsorption of oxygen and subsequent chemical analysis using the iodometric method; (b) for the experiments with adsorption of oxygen and subsequent analysis using the hydrazine method.

$$Me^{3+} + Cl^- = Me^{2+} + \tfrac{1}{2}Cl_2$$

(Me^3 stands for Ni^{3+} or Co^{3+} ions), was removed from vessel 1 by a current of nitrogen and introduced into the KI solution where an equivalent amount of free iodine was formed. The iodine was subsequently titrated with 0.01 N solution of $Na_2S_2O_3$. From the results, the amount of Ni^{3+} or Co^{3+} ions present in the sample after adsorption of oxygen was calculated. This calculation was made on the assumption that hydrochloric acid may be oxidized only by Ni^{3+} or Co^{3+} ions and none of the adsorbed oxygen species may react with it. In particular we assumed that, in the course of the dissolution of the sample, the surface of which was covered with chemisorbed oxygen, disproportionation of negative adsorbed oxygen ions took place, e.g., according to the equations:

$$2O_2{}^-{}_{(ads)} + 2H_3O^+ = 3H_2O + \tfrac{3}{2}O_2,$$
$$2O^-{}_{(ads)} + 2H_3O^+ = 3H_2O + \tfrac{1}{2}O_2.$$

This assumption was verified in a series of experiments in which it was proved that, besides chlorine, free oxygen also evolves while dissolving oxygenated samples in hydrochloric acid. The description and discussion of these experiments is given in the Appendix.

As already stated, in several runs after adsorbing a given amount of oxygen, analytical determinations of surface excess oxygen were carried out using the hydrazine method proposed by Uchijima *et al.* (*15*). In this method, the sample, the surface of which is covered with adsorbed oxygen, is treated with a solution of hydrazine. The amount of hydrazine oxidized in these conditions is taken as the measure of the amount of surface excess oxygen. Uchijima *et al.* (*15*) assumed the following reaction:

$$N_2H_4 + 2O_{(ads)} = N_2 + 2H_2O.$$

It was, however, not clear which forms of adsorbed oxygen react with hydrazine. To elucidate this point we used the apparatus already described, only with the difference that reaction vessel 1 had the form shown in Fig. 2b. The narrow part of the vessel supported a sealed glass bulb B containing 2–3 cm^3 of 0.3 N hydrazine solution outgassed before sealing. The NiO samples were prepared as previously by thermal decomposition of $Ni(OH)_2$, the heating device being situated in such a position that the bulb with the solution was kept practically at room temperature. After a given amount of oxygen had been adsorbed on the sample, reaction vessel 1 was immersed in liquid nitrogen, and the bulb with the N_2H_4 solution was broken with a steel rod sealed in glass tubing *P* and operated with the help of an external magnet. The Dewar vessel with liquid air was then slowly removed, the frozen liquid again thawed and reacted with the chemisorbed oxygen, as was manifested by the evolution of small gas bubbles and also by the regaining of a light green color by the sample, which always blackened in the course of chemisorption of oxygen. The solution was again frozen with liquid nitrogen and the gas (N_2) which was evolved was pumped out with the mercury diffusion pump 2 into the calibrated volume between the diffusion pump 2 and taps K_3, K_4, and K_5. Now the volume was cut off by tap K_1 and the solidified solution of hydrazine again was liquified and warmed to room temperature The new portion of evolved nitrogen was again pumped out after freezing the solution to the calibrated volume, and so on. The cycles of such operations were repeated until a constant nitrogen pressure in the calibrated volume was reached. In a series of additional experiments, after measuring the amount of nitrogen, its purity was checked. The calibrated volume was connected with an evacuated vessel containing a little stoichiometric nickel oxide of high surface area prepared as previously. It never blackened nor even darkened and the fact that its yellow-green color remained unchanged proved the absence of oxygen.

RESULTS AND DISCUSSION

Adsorption of Oxygen on NiO and CoO

The results with nickel oxide are presented first. The data given in Table 1 correspond to the experiments carried out at room temperature. Oxygen gas introduced into the reaction vessel remained in contact with the NiO sample for 10 min. After this period, it was evacuated into the calibrated volume; and then the analytical determination of the number of Ni^{3+} ions was carried out. Table 1 shows that about 90% of the adsorbed oxygen was adsorbed irreversibly, which is very similar to the results obtained by Kuchynka and Klier (*1*). From the analytical determination the ratio of the number of Ni^{3+} ions to the number of irreversibly adsorbed O atoms was calculated and given in column 6 of Table 1. It is very close to unity, which formally may correspond to the presence of O_2^{2-}, O^- ions or to the formation of O_2^- and O^{2-} species in equal proportions. The peroxide ion O_2^{2-} has strongly negative bond energy [−125 kcal/mole according to Tuck (*17*)] and can only be stabilized in salts with highly electropositive metals (Li–Cs, Ca–Ba). Evidently no such stabilization may be expected on the surface of NiO and

TABLE 1

NiO: ADSORPTION–DESORPTION–ANALYSIS (room temp)

Wt of $Ni(OH)_2$ sample (g)	Oxygen (μmoles of O_2) Total adsorbed	Desorbed	Adsorbed, remaining after desorption	Ni^{3+} ions in NiO (μmoles of Ni^{3+})	Ratio [Ni^{3+} ions: irreversibly adsorbed oxygen atoms (Ni^{3+}/O_{ads}; no.)]	Oxygen reversibly adsorbed (%)
0.100	2.32	0.19	2.12	4.32	1.02	8.4
0.100	2.16	0.25	1.90	3.85	1.01	11.4

this form of chemisorbed oxygen must be rejected. The simultaneous formation of O_2^- and O^{2-} in equal proportions is much less probable than the formation of O^-. Against such possibility speaks the fact that, as shown below, the process of acquiring a mean electrical charge of adsorbed O atoms higher than one (the process unambigously connected with the formation of O^{2-} species) which is relatively fast at 235°C, slows down very much at 150°, and must be very slow at room temperature, at which irreversible sorption resulting in the formation of oxygen species with mean electrical charge -1 is very fast. There is also no obvious reason why O^{2-} and O^- species should be produced in equal proportions at various experimental conditions. We arrive therefore at the conclusion that oxygen irreversibly adsorbed on nickel oxide is present at room temperature and at low coverages in the form of O^- ions.

The next experiments were carried out in the same conditions as those already described only with the difference that no desorption of oxygen primarily adsorbed was carried out. The surface of the NiO sample dissolved in hydrochloric acid was therefore covered with irreversibly as well as reversibly adsorbed oxygen. The data in Table 2, column 2 show that similar total amounts of oxygen were adsorbed as in the experiments listed in Table 1 and in spite of not carrying out desorption of reversibly adsorbed oxygen the number of Ni^{3+} ions was also very similar to the previous result. It shows, therefore, that the reversible adsorption of oxygen on nickel oxide is not accompanied by the formation of Ni^{3+} ions, i.e., by electron transfer from the adsorbent to the adsorbate molecules. Such a conclusion is in perfect agreement with the measurement of electrical conductivity carried out by Marcellini *et al.* (*2*) and by Kuchynka and Klier (*1*). Assuming that each Ni^{3+} ion in NiO corresponds to the formation of one O^- (ads), we could calculate the percentages of oxygen irreversibly and reversibly adsorbed from the data in Table 2, columns 2 and 3. The latter values (given in Table 2, column 5) are in good agreement with the direct determinations, the results of which are given in Table 1.

It followed from the measurements of Kuchynka and Klier that the ratio of the amounts of reversibly and irreversibly adsorbed oxygen changes with time. In order

TABLE 2

NiO: ADSORPTION–ANALYSIS (room temp)

Wt of $Ni(OH)_2$ sample (g)	Total adsorbed oxygen (μmoles of O_2)	Ni^{3+} ions in NiO (μmoles Ni^{3+})	Ratio [Ni^{3+} ions: total adsorbed oxygen atoms (no.)]	Oxygen reversibly adsorbed calculated from data in columns (2) and (3) (%)
0.100	2.42	4.38	0.904	9.6
0.100	2.33	4.30	0.920	8.5

to collect more information about this process, we carried out a series of experiments the results of which are given in Table 3. A sample of 0.1 g of $Ni(OH)_2$ was decomposed; and 4.79 μmoles of O_2 were introduced into the reaction vessel at room temperature. After 26 min, 3.05 μmoles of O_2 were adsorbed. The reaction vessel was then evacuated into the desorption volume. Oxygen (0.93 μmoles) was desorbed, showing that (after 26 min) 2.12 μmoles (64.9%) were adsorbed irreversibly. The reaction vessel and desorption volume were then reconnected and oxygen could be readsorbed. After 3 hr and 20 min from the very beginning of the experiments, the total amount of adsorbed oxygen was 3.58 μmoles. In the next desorption, 0.59 μmoles of oxygen were desorbed and the amount of irreversibly adsorbed oxygen increased up to 2.99 μmoles. As the results presented in Table 3 show, on reiterating adsorption–desorption cycles in periods of some 20 hr or more, we found a gradual increase in the amount of total adsorbed oxygen and simultaneously an increase in the proportion of irreversibly adsorbed oxygen. After 92 hr and 20 min, all the oxygen was irreversibly adsorbed; and no further desorption could be effected. Iodometric analysis, carried out at this stage, showed a number of Ni^{3+} ions in NiO, which corresponded to the average transfer of 1.1 electrons per 1 adsorbed O atom. Such a result shows that the O^- form of irreversibly adsorbed oxygen still remained the predominant form after a period of 4 days. The departure from the strict value 1 of the $Ni^{3+}/O(ads)$ ratio might indicate that about 10% of O^- ions turned into O^{2-} ions and in this form became incorporated into the NiO crystal lattice. It should, however, be observed that the total amount of adsorbed oxygen given in Table 3 has been calculated as the sum of six successive determinations and is therefore definitely less exact than the result of a single determination. The standard deviation in the determination of $Ni^{3+}/O(ads)$ ratio in the single experiment as reported in Table 1 was estimated to be about 2% and the maximal possible error of the determination about 5%.

TABLE 3

NiO: REPEATED ADSORPTION–DESORPTION CYCLES (room temp)

Time (hr) (min)	Amount of oxygen (μmoles): Total adsorbed	Desorbed	Adsorbed, remaining on surface after desorption
26	3.05	0.93	2.12
3 21	3.58	0.59	2.99
19 40	4.24	0.19	4.06
43 20	4.60	0.09	4.51
66 20	4.72	0.04	4.67
92 20	4.79	0.00	4.79

Although the incorporation of oxygen into the NiO lattice at room temperature was not certain, there was no doubt about it in the course of subsequent experiments carried out at elevated temperatures.

Table 4 shows the results obtained in the course of experiments in which adsorption of oxygen took place at 150 and 235°C. In both cases, only irreversible adsorption was observed. No oxygen could be desorbed after the introduction of the gas into the reaction vessel at 150°C and after 10 min the O^- form was practically the only species of adsorbed oxygen. The prolongation of the period of time in which the sample remained covered with adsorbed oxygen up to 120 min resulted in the transformation of nearly 44% of O^- into O^{2-} ions. After 240 min, 52% of the oxygen was present in the form of O^{2-} ions. The velocity of the $O^- \rightarrow O^{2-}$ transformation was still higher at 235°C, when, after 8 min, 21.7% of the adsorbed oxygen was already incorporated into the lattice in the form of O^{2-} ions. These results are in good accordance with those obtained by Dereń and Nowotny *(10)* and Chruściel *et al* *(9)*, who observed distinct changes in the electron work function during adsorption of oxygen on NiO at elevated temperatures.

High surface area stoichiometric cobalt oxide (CoO) showed a stronger tendency to bind oxygen irreversibly than did nickel oxide. No desorption of adsorbed oxygen

TABLE 4
NiO: ADSORPTION (irreversible)-ANALYSIS (150 and 235°C)

Wt of $Ni(OH)_2$ sample (g/min)	Time of adsorption (min)	Temp (°C)	Total adsorbed oxygen (μmoles of O_2)	Ni^{3+} ions in NiO (μmoles of O_2)	Ratio [Ni^{3+} ions (no.): total (amount) adsorbed oxygen (Ni^{3+}/O_{ads})]
0.100	10	150	2.84	5.76	1.02
0.100	10	150	2.84	5.56	0.98
0.100	120	150	2.57	7.37	1.44
0.100	240	150	1.33	4.04	1.52
0.100[a]	8	235	2.94	7.21	1.23
0.100[a]	8	235	2.99	7.28	1.22

[a] NiO sample obtained by decomposition of $Ni(OH)_2$ at 235°C.

could be observed at room temperature if the evacuation started 10 min after the gas had been introduced into the reaction vessel. The data in Table 5 show that, after that time, the $Co^{3+}/O(ads)$ ratio was 1.85 and 1.89. Therefore, it follows that, in this case, the predominant oxygen form was O^{2-}. Only 15 and 11% respectively of the adsorbed oxygen atoms were present in the form of O^- ions. This result shows that, at room temperature, oxygen already becomes incorporated into the lattice of high surface area CoO, which is in good accordance with the fact that preparations of CoO obtained by thermal decomposition of carbonate *in vacuo* violently absorb oxygen from the air, with a marked development of heat and pass into the Co_3O_4 phase. However, it should be observed that, in the course of our experiments, no sintering of CoO took place. In one of our experiments, the BET surface areas before and after adsorption of oxygen were found to be 91 and 93 m^2/g respectively.

TABLE 5
CoO: ADSORPTION (irreversible) ANALYSIS (room temp)

Wt of $CoCO_2$ sample (g)	Total adsorbed oxygen (μmoles of O_2)	Co^{+3} ions in CoO (μmoles of Co^{+3})	Ratio [Co^{+3} ions: total adsorbed oxygen atoms (Co^{+3}/O_{ads}; no.)]
0.100	5.12	19.00	1.85
0.100	5.08	19.18	1.89

Determinations of Surface Oxygen Using the Hydrazine Method

The results concerning the simultaneous determination of adsorption of oxygen on nickel oxide and the determination of surface oxygen by means of the hydrazine method are given in Table 6. Adsorption of oxygen took place at room temperature and chemical analysis was carried out 12 min after the gas had been introduced into the reaction vessel. As shown above, in the same conditions, about 90% of the oxygen is adsorbed irreversibly in the form of O^- ions and about 10% reversibly. Table 6 shows that the number of micromoles of liberated nitrogen was very close to the total number of micromoles of adsorbed oxygen. The hydrazine is therefore oxidized by reversibly adsorbed oxygen, as well as by O^- adsorbed ions.

CONCLUSIONS

With NiO, electron transfer accompanies only the irreversible adsorption of oxygen. Reversibly adsorbed oxygen (molecular chemisorption according to Klier and Kuchynka) is electrically neutral. For high surface area NiO preparations, the ratio of the number of Ni^{3+} ions to the number of irreversibly adsorbed oxygen atoms is very close to unity if the experiments are carried out at room temperature. This result indicates that chemisorbed oxygen is present in the form of O^- ions on the surface of NiO. At 150°C, no reversible adsorption of oxygen could be detected.

TABLE 6

NiO: Adsorption Analysis by Using the Hydrazine Method (room temp)

Wt of $Ni(OH)_2$ sample (g)	Total adsorbed oxygen of (μmoles of O_2)	Nitrogen evolved in reaction with N_2H_4 (μmoles of N_2)
0.200	0	0
0.100	4.55	4.85
0.100	1.79	1.88
0.100	1.50	1.44
0.100	2.16	2.17

Oxygen is adsorbed at first in the form of O^- ions which slowly turn into O^{2-} ions and become incorporated into the NiO lattice. At 235°C, the velocity of incorporation of oxygen into the bulk is very much faster.

High surface area cobaltous oxide behaves somewhat differently. No reversible adsorption of oxygen could be detected at room temperature, and it was predominantly adsorbed in the form of O^{2-} ions (incorporation). In the conditions used in the present research, only 10–15% of oxygen remained in the form of O^- ions after 10 min.

Appendix

As mentioned above, when calculating the results of iodometric determinations, the assumption was made that the hydrochloric acid in which the sample covered with adsorbed oxygen was dissolved was oxidized only by Ni^{3+} and Co^{3+} ions respectively, and not by any form of adsorbed oxygen. In particular, it has been assumed that oxygen chemisorbed in the form of O^- ions is disproportionated when the sample is dissolved in hydrochloric acid:

$$2O^-_{(ads)} + 2H_3O^+ = 3H_2O + \tfrac{1}{2}O_2.$$

If this assumption is true, the dissolution of an NiO sample (the surface of which is covered with 1 mole of oxygen adsorbed in the form of O^- ions) should be accompanied by the evolution of 0.5 mole of gaseous oxygen.

In our experiments to test this assumption, we first confirmed the evolution of oxygen and then determined its content. In the first series of experiments, samples of 0.1 g of $Ni(OH)_2$ (sample I) were decomposed *in vacuo* and a portion of oxygen was adsorbed on their surfaces at room temperature. After 10 min, the reversibly adsorbed oxygen was removed by pumping it out to the calibrated volume. The reaction chamber was then cut off, filled with oxygen-free nitrogen gas, and then thoroughly outgassed hydrochloric acid was introduced. The apparatus was modified in such a way that, using a system of break-off glass seals, it was possible, in the course of dissolution of the sample in the acid, to carry off the oxygen and chlorine in the nitrogen stream to the thoroughly outgassed solution of KI. The current of nitrogen was subsequently directed to a liquid air trap and then to a volume containing another sample of high surface area nickel oxide (sample II) showing the typical yellow-green color. In contact with nitrogen coming from the vessel where the NiO sample I was dissolved, the NiO sample II blackened, which was a signal showing that free oxygen was present in the system. In order to have some orientation as to the amount of oxygen carried to NiO sample II, we determined the number of Ni^{3+} ions in it. In three successive determinations, it amounted to 47.6, 38.6, and 27.8% of the number of Ni^{3+} ions detected in NiO sample I. However, the experiments could be treated as semiquantitative only because of the fact that, in the given conditions, the volume of the carrier gas was not large enough to carry off the oxygen evolved in the course of dissolving sample I quantitatively from the reaction chamber to the vessel containing NiO sample II.

Quantitative determinations of the amount of oxygen evolved in the course of dissolving the sample were carried out, in a similar way to the experiments described on the hydrazine determinations, with the difference that the sealed glass bulb was filled with hydrochloric acid solution destined to dissolve the NiO sample covered with irreversibly adsorbed oxygen. After dissolving the sample in the boiling hydrochloric acid solution the liquid was frozen at liquid nitrogen temperature; and

TABLE 7
NiO (room temp)

Wt of $Ni(OH)_2$ sample (g)	Oxygen (μmoles) Adsorbed irreversibly	Oxygen (μmoles) Evolved in reaction with HCl	Ratio [oxygen adsorbed: oxygen evolved in reaction with HCl; (amount)]
0.100	0.76	0.41	1.86
0.100	0.74	0.39	1.90
0.100	1.84	0.94	1.95
0.150	2.36	1.26	1.87
0.100	0.97	0.47	2.07
Mean			1.93 ± 0.08

the gaseous oxygen evolved in the reaction chamber was pumped out by the intermediation of a liquid air trap (condensation of chlorine) to the calibrated volume, where its pressure was measured by means of a Pirani gauge. The amounts of oxygen irreversibly adsorbed and detected after dissolving the sample are given in Table 7. The expected ratio of both, amounting to 1.93 ± 0.08 confirms quantitatively our assumption about the behavior of O^- adsorbed species in the course of dissolving a sample.

The eventuality that, in the conditions of our experiments, oxygen had been formed in the secondary reaction,

$$Cl_2 + H_2O = 2H^+ + 2Cl^- + \frac{1}{2}O_2,$$

was checked by experiments in which, instead of NiO, samples about 1 mg of $KMnO_4$ were introduced into the reaction chamber, and, after evacuation, dissolved in boiling hydrochloric acid in the above-described manner. After freezing the liquid at the temperature of liquid nitrogen and pumping the reaction chamber, no increase of pressure could be registered in the calibrated volume thus showing that no evolution of oxygen took place.

Using the same apparatus, a series of experiments was also carried out in which nickel oxide samples prepared *in vacuo* in the usual way were dissolved in hydrochloric acid without previously adsorbing oxygen at their surfaces. In these conditions no formation of gas not condensing at liquid nitrogen temperature took place. It follows therefore that, the NiO samples did not contain metallic nickel, since in that case, evolution of hydrogen would have occurred.

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