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Studies of Surface Reactions of NO by Isotope Labeling

VII. Oxygen Exchange Between Nickel Oxide and $N^{18}O$, $^{18}O_2$ and $N_2{}^{18}O$

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Previously it was found that Fe_2O_3 exchanges oxygen with nitric oxide at temperatures far below those required for the decomposition of NO. This work extends the study to NiO.

A comparison is made between the exchange of oxygen in the surface of NiO single crystals with $N^{18}O$, $^{18}O_2$ and $N_2{}^{18}O$. Exchange of oxide oxygen with NO is measurable at room temperature, while the exchange with O_2 begins at 200°C; N_2O exchanges its oxygen even more slowly than does molecular oxygen and, unlike NO, tends to decompose before the oxygen exchanges.

INTRODUCTION

In a previous study, oxygen exchange between the surface of Fe_2O_3 and gaseous NO was found to take place at temperatures far below the range where decomposition of nitric oxide is noticeable (*1*). This study has been extended to NiO, which is of interest because it is a good oxygen-transfer catalyst. In addition, small single crystals of NiO can be prepared with sufficient surface area to allow accurate determination of exchange rates.

The catalytic behavior of NiO, like that of other transition metal oxides, is strongly influenced by a number of subtle changes in the surface structure, such as the oxidation state, the level of contaminants, the particle size and the exposed crystal face. To elucidate this behavior, the exchange of oxide oxygen with the oxygen of different gaseous molecules was studied on several samples of NiO. Among these samples were well-defined single crystals with an exposed (111) face, the same crystals after crushing, and polycrystalline powders of two different grades of purity.

The main purpose of this work was an investigation of the oxygen exchange between NO and the surface of NiO. In addition, a similar study of the NiO–O_2 system was made, as it was of interest to compare the exchange properties of two differently bonded oxygen atoms. Moreover, since the NiO–O_2 exchange has been studied by several investigators (*2–5*) it is possible to compare our NiO samples with samples prepared in other laboratories. Such a comparison is instructive, as, depending on the preparation, NiO surfaces of widely different activity can be obtained.

The N_2O molecule, in contrast to NO, is known to yield its oxygen atom with ease. For this reason, some experiments of the NiO–N_2O exchange were also performed.

EXPERIMENTAL SECTION

NiO Samples

a. Polycrystalline NiO, specpure (SP). This sample, a spectrographic grade NiO (Johnson, Matthey and Co., Ltd.) contained the following impurities (in parts

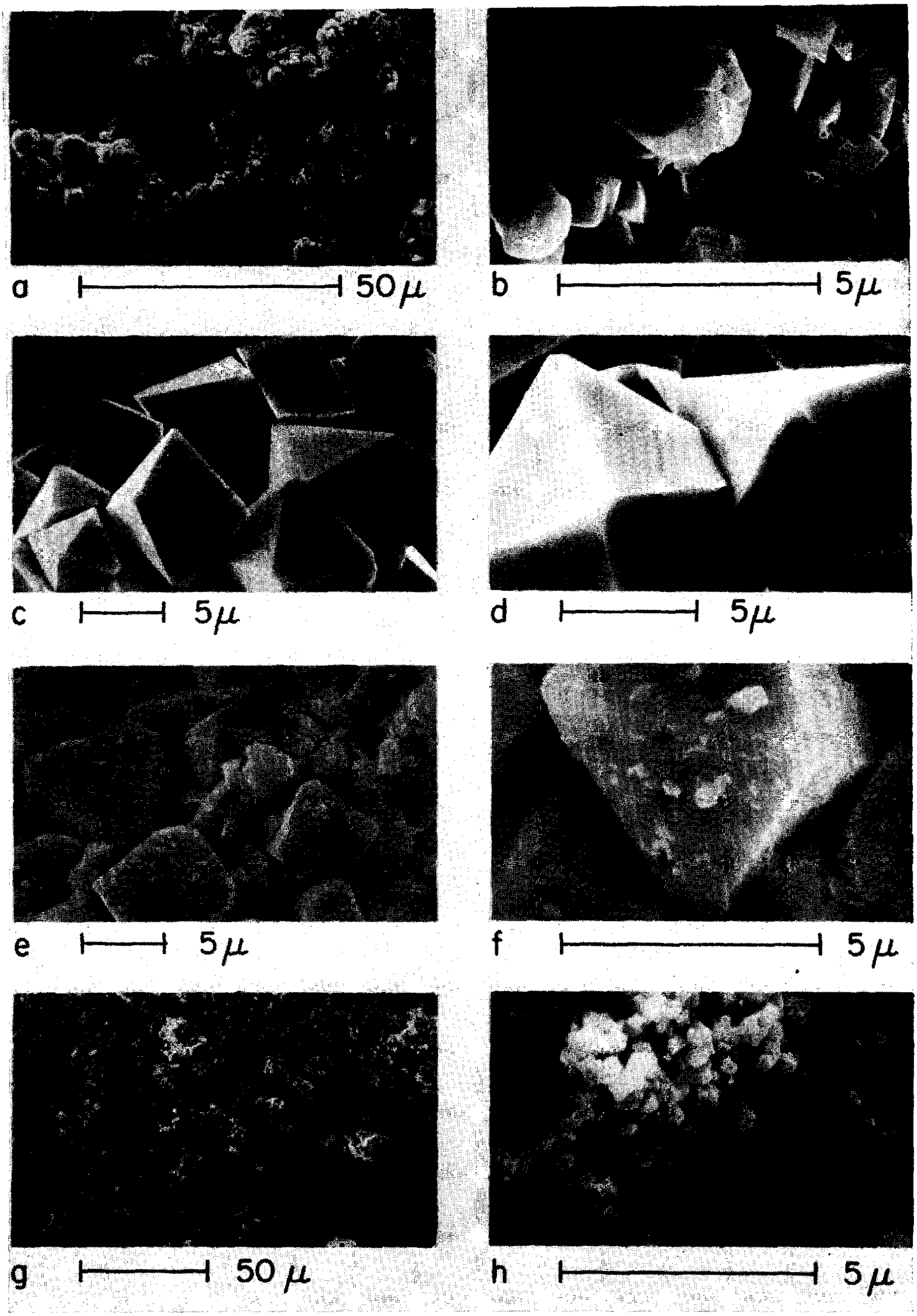

FIG. 1. Electron micrographs of the NiO samples used in the exchange studies.

per million): Fe 5, Si 2, Cu 1, Al, Ca, Mg and Ag < 1. Since some CO_2 was released when this NiO was heated in vacuo or treated with oxygen, a combustion analysis was performed, indicating 100 ± 20 ppm of C. Gravelle and Teichner (*5*) have pointed out that a nearly stoichiometric nickel oxide may contain small quantities of metallic nickel, especially if it is prepared in vacuo above 300°C. On one occasion this problem was encountered in a batch of the specpure material which contained particles attracted by a small horseshoe magnet. All the samples which were actually used in the exchange studies, however, were free of metallic nickel, as shown by X ray diffraction.

Micrographs of this powder are given in Figs. 1a and 1b. The particles do not exhibit a regular shape, but some facets are discernible in Fig. 1b, suggesting that an appreciable portion of the surface consists of low index planes.

b. Single Crystals of NiO (SC). To obtain single crystals, the specpure powder was recrystallized in a melt of sodium tetraborate (*6*) by the following procedure: 45 g of NiO were mixed thoroughly with 84 g of anhydrous $Na_2B_4O_7$ (reagent grade, Matheson, Coleman and Bell) and fused in a platinum crucible at 1050°C for at least 8 h. The crucible was removed from the furnace and cooled to room temperature. The flux component was dissolved by boiling the solidified melt in 25% nitric acid for several hours. The recovered NiO single crystals were washed several times in distilled water, and dried in air at 100–150°C. Electron micrographs, reproduced in Figs. 1c and 1d, show that the crystals exhibit a well-defined octahedral habit. The formation of the (111) crystal face is preserved even in those instances where twinning occurred, Fig. 1d. The crystals used in the study were −200 mesh (<74 μm). Most of the crystals passed through the screen and were used in this form. Figure 1c is fairly representative of the particle size. An average octahedron edge of 8.2 μm was estimated from the specific surface area and the NiO density.

The process of recrystallization did not introduce additional contaminants. The only difference, found by spectrographic analysis, was an increase of the Na level from below 100 ppm to 200 ppm. Possible contamination by Pt (*6*) was avoided by a coating of NiO crystals on the crucible walls. This coating of large NiO crystals was formed by repeated recrystallization of the melt and adhered strongly to the Pt surface. These crystals were not easily removed when treated with dilute HNO_3.

c. Fractured single crystals of NiO (FC). The coarser single crystals (>74 μm) were crushed in an agate mortar to produce a surface with different crystal faces. It was difficult to fracture the single crystals completely. The micrographs in Figs. 1e and 1f demonstrate the results of the crushing. A substantial amount of the original octahedral plane still remains intact. However, a closer inspection at larger magnification shows that the octahedral surfaces lost their smooth appearance and were severely pitted (Fig. 1f).

d. Polycrystalline NiO, reagent grade (PC). This NiO (J. T. Baker) was of lower purity (99.5%) and contained the following major impurities (in parts per million): Pb 1000, Na 1000, Mo 1000, Zn 500, Si 500, Co 300 and Mg 100. Combustion analysis showed the presence of 220 ppm of C. This powder had a much smaller particle size than the other samples, as shown by the micrographs in Figs. 1g and 1h.

The surface areas of the four samples a–d (designated SP, SC, FC and PC, respectively) as measured by Ar adsorption (*7*), are given in Table 1.

TABLE 1

SPECIFIC SURFACE AREAS OF NiO SAMPLES

Designation	Description	BET area (m^2/g)
SP	Specpure material before recrystallization	0.205
SC	Single crystals	0.120
FC	Fractured single crystals	0.275
PC	Polycrystalline powder analytical grade	1.77

Isotopes

The isotopes employed for the exchange experiments were $N^{18}O$ (isotopic purity 94.6%, International Chemical Nuclear Corp.), $^{18}O_2$ (isotopic purity 97.9%, Weizmann Institute, Israel), and $N_2{}^{18}O$ (isotopic purity 88.4%, Prochem Ltd., U.K.).

Apparatus

Details of the reactor, the mercury-free circulation apparatus and the mass spectrometric analyses have been given earlier (*8*). As higher temperatures were required in some instances, a Vycor reactor was used. The gas analyses were performed by a CEC 21-614 mass spectrometer, into which small samples (<1 cm³) were injected directly from the circulation batch reactor.

Experimental Procedure

The isotopes were diluted with Ar in a 2-liter bulb to 0.6–0.7 vol%. The Ar served both as a carrier gas and as an internal standard for the mass spectrometric analyses. For each experiment 150 Torr of the mixture was admitted to a circulation volume of about 350 cm³, including the reactor. This quantity corresponds approximately to 16 μg-atom, or 9.6×10^{18} atoms, of ^{18}O in the cases of NO and N_2O, and twice that amount in the case of O_2. The NiO sample size was always chosen to have a surface area of 1 m². As the nominal density of oxygen atoms in the (111) plane of stoichiometric NiO amounts to $13.2 \times 10^{18}/m^2$, the amount of the ^{18}O isotope in the gas phase was of the same order of magnitude as the amount of ^{16}O in the sur-

TABLE 2
Comparison of Published NiO–O_2 Exchange Rates

Source and pretreatment of sample	Surface area (m²/g)	Experim. conditions		Activ. energy (kcal/mole)	Reaction order	Normalized exchange rate (300°C, 1 Torr) atoms/(m²·s)	Ref.
		Torr	°C				
$Ni(NO_3)_2$ vacuum at 520°	3.12	10	300	35	0	3.9×10^{14}	(3)
$Ni(NO_3)_2$ 15 Torr O_2 370° brief evacuation	6.04	10	300	45	0.2	1.6×10^{13}	(3)
$Ni(OH)_2$ decomposition 200°	156	24	250	15	0	2.4×10^{14}	(9)
$Ni(OH)_2$ decomposition in air at 500°	7.8	10	300	—	0	1.7×10^{17}	(10)
$Ni(OH)_2$ decomposition in air, 500° evacuation at 200°	7.7	40	300	24	0.4	4.6×10^{15}	(11)[a]
$NiCO_3$ air at 850° evacuation at 400°	5.5	40	300	—	—	3.8×10^{14}	(12)[a]
$NiCO_3$ decomposition in air, 800°	5.4	40	350	32	0.4	1.1×10^{14}	(13)[a]
$NiCO_3$ decomposition in air, 1200°	1.3	40	350	40	0.5	2.5×10^{13}	(13)[a]
SC described here, O_2 and evacuation at 400°	0.12	1	297	23	—	7.8×10^{13}	This work
PC described here same treatment, 400°	1.8	1	417	23	—	6.8×10^{12}	This work

[a] These rates were derived from the homomolecular exchange, and are equal to the initial rates of exchange between molecular oxygen and oxide oxygen of NiO (*11*).

face of the solid sample. A fresh sample of NiO was used for each exchange experiment.

Results and Discussion

Published experimental data of the exchange between molecular oxygen and NiO surfaces (*3, 9–13*) are given in Table 2. To permit a direct comparison only data which can be normalized to 300°C and 1 Torr are included. The first column briefly describes the sample preparation. The specific surface areas of the samples, and the oxygen pressure and temperature of the exchange are listed in columns 2–4. The next two columns give the energies of activation and the reaction orders used to normalize the exchange rates which are given in the next column. The appropriate references are given in the last column. In those cases where a sufficient description is given by the references these rates were measured during the initial stage of the exchange. The large variations of the data in Table 2 are mainly caused by differences in sample preparation, but it is not easy to discern a consistent trend of the exchange rate as a function of temperature and oxygen pressure, used in preparing the different samples. Moreover, details of the pretreatment are not always clearly stated. The data scatter emphasizes that extreme care must be taken to produce a well-defined surface state of NiO, which is essential for a meaningful comparison of different oxygen exchange experiments.

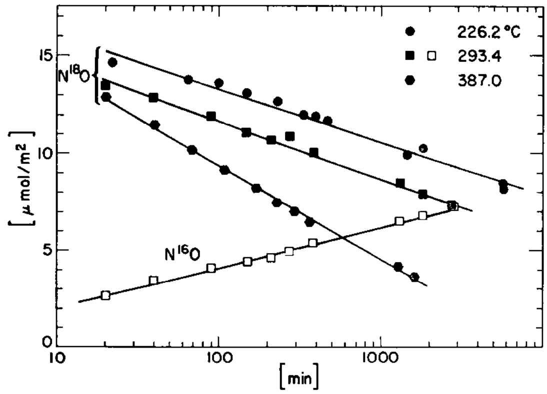

FIG. 2. NiO–NO exchange isotherms of sample PC in the temperature range 225–390°C.

NiO–NO Exchange

a. Surface after rigorous evacuation. To establish that the exchange actually takes place with oxygen from the oxide lattice, and not from a chemisorbed phase, the samples of NiO were evacuated thoroughly. In one series of experiments, NiO of PC type was evacuated overnight at 400°C by a VacIon pump at a residual pressure of $<5 \times 10^{-6}$ Torr. Results of the exchange between NO and this NiO surface are shown in Fig. 2. The amount of $N^{18}O$ in the gas phase at 226, 293, and 387°C, and the appearance of $N^{16}O$ at 293°C, given for comparison, are plotted as a function of time. The time scale is logarithmic because of the long duration of the experiment. As presented, the plots are linear. The material balance at the end of the exchange at 293°C shows a loss of NO ($N^{16}O + N^{18}O$) of 2.1 μmole. This amount can be explained by NO chemisorption in accordance with earlier adsorption results (*14*). Obviously it is not known to what extent the adsorbed NO has exchanged its oxygen with the surface.

The SC sample, exposed to the same evacuation at 400°C became severely deficient in surface oxygen. Thus, the sample reduced $N^{18}O$, which was admitted at 385°C, with the liberation of N_2 and incorporation of the ^{18}O into the solid. This fact by itself is sufficient to indicate that the surface oxygen of the SC sample is more labile than that of the PC sample. To be able to follow the oxygen exchange on the SC crystals, while keeping the surface as free as possible of chemisorbed oxygen, the temperature of the overnight evacuation was lowered to 250°C. Figure 3 shows the result of the exchange experiment at 165°C. The lower temperature indicates the ease of the exchange on the SC crystals as compared to the PC sample. In contrast to the linear plots of the PC sample (Fig. 2), the SC sample yields sigmoid shaped curves. The appearance of $N^{16}O$ matches the disappearance of $N^{18}O$ within 3% of a monolayer (0.74 μmole).

b. The influence of chemisorbed oxygen. The variation of the exchange rate, for a given sample, induced by different pretreat-

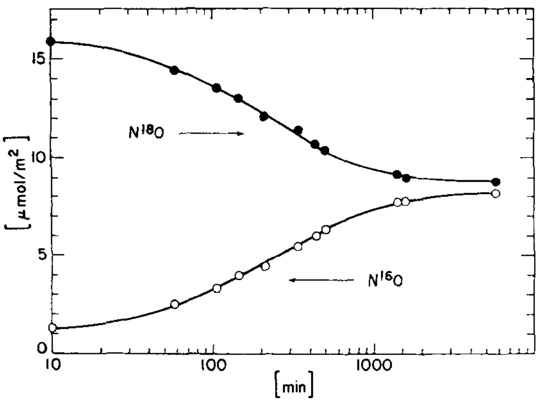

Fig. 3. NiO-NO exchange isotherms of sample SC at 165.1°C.

ments, is illustrated in Fig. 4. The first SC sample (square symbols) has been kept in vacuo at 250°C overnight. The second SC sample (round symbols) was exposed to 1% of natural oxygen in Ar at 400°C overnight, followed by a short evacuation at the exchange temperature of 225°C. The rapid initial exchange on the second sample is clearly due to an excess of oxygen on the surface. Figure 4 is plotted in ordinary Cartesian coordinates, since the duration of the experiment was short. Note that in the second case the amount of $N^{18}O$ in the beginning (17.5 μmole) was somewhat higher than in the first case (15.9 μmole).

c. Oxygen pretreatment followed by brief evacuation. Identical sample pretreatment, as mentioned before, is essential for a quantitative comparison of exchange rates. Such a common pretreatment was experimentally established, which, on one hand did not lead to NO reduction on the single crystals, as mentioned under (a), and on the other hand, did not result in excessive NO chemisorption. For this purpose the samples were exposed to 1% of natural oxygen (in Ar) overnight at 400°C, evacuated at the same temperature for 30 min, and then cooled quickly to the exchange temperature. This specific surface treatment was applied to all the samples used in the exchange experiments with the three oxygen containing gases, described hereafter. The exchange rates after this pretreatment were found to agree with those obtained after overnight evacuation at 400°C in the case of PC NiO, and overnight evacuation at 250°C in the case of SC NiO. A comparison of initial exchange rates at 300°C and 1 Torr, extrapolated from 293°C for the PC sample, and from 165°C for the SC sample, are 9.3×10^{14} and 7.5×10^{15} oxygen atoms/($m^2 \cdot s$), respectively. These values permit a quantitative comparison with the slower NiO–O_2 exchange rates (cf. Table 2), although extrapolation in the case of the SC sample may introduce a sizable error. The exchange on the single crystals was measurable at temperatures as low as 25°C. At this temperature, 16% of a monolayer of ^{16}O atoms had been replaced by the ^{18}O isotope after 6000 min.

The apparent energy of activation at the point where 0.2 of a monolayer has been exchanged is almost the same on the SC sample (14.5 kcal/mole) and on the PC

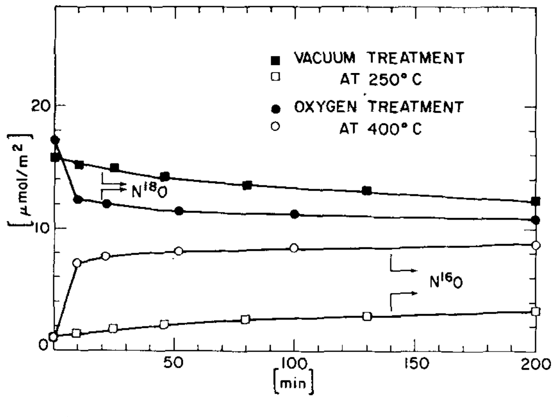

Fig. 4. Comparison of NiO–NO exchange at 225°C for different pretreatments of sample SC.

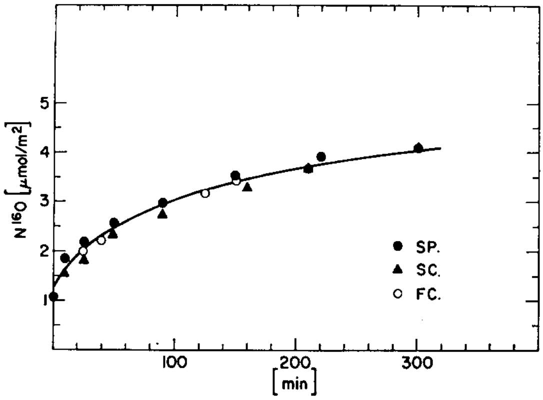

FIG. 5. Comparison of NiO–NO exchange at 115°C on samples SP, SC and FC.

sample (12.5 kcal/mole). It is difficult to determine an energy of activation in the very beginning of the exchange.

d. Influence of crystal face. For an elucidation of the effect of the crystal face on the exchange rate, specpure powder (SP), single crystals (SC) and fractured crystals (FC) were employed at an exchange temperature of 115°C. The appearance of $N^{16}O$ per unit area is used in Fig. 5 as a measure of the exchange. All the points of the three samples of exactly the same chemical composition are well-described by a common curve, indicating that the effect of the exposed crystal face, if any, is not substantial.

e. Exchange kinetics. The oxygen exchange between NO and the surface of an oxide is given by

$$N^{18}O + (^{16}O)_s = N^{16}O + (^{18}O)_s. \quad (1)$$

Under our experimental conditions decomposition, reduction and surface retention of NO can be neglected. Furthermore we are here not interested in the homomolecular exchange between NO molecules (*1, 15*).

Based on the notations of Nováková (*16*), used to describe the exchange between molecular oxygen and oxide oxygen, the rate of the NiO–NO exchange can be expressed as

$$dq/dt = R(vw - uq), \quad (2)$$

where $q(t)$ is the number of $N^{16}O$ molecules in the gas phase, $u(t)$ is the number of ^{18}O atoms in the solid, $v(t)$ is the number of exchangeable ^{16}O atoms in the solid, $w(t)$ is the number of $N^{18}O$ molecules in the gas phase, and R is a constant. The values of u, v, and w are functions of time and can be eliminated by introducing three time-independent constants: the total number of NO molecules in the gas phase $a = q + w$, the total number of ^{16}O atoms $b = q + v$, and the total number of exchangeable oxygen atoms in the solid $m = u + v$. Thus, it follows

$$dq/dt = R(a + m) \cdot (ab/(a + m) - q). \quad (3)$$

The equilibrium is reached when the exchange stops, $dq/dt = 0$; this happens at infinite time and according to Eq. (3), when $q = ab/(a + m) \equiv q_\infty$. Equation (3) can be rewritten

$$dq/dt = R(a + m)(q_\infty - q). \quad (4)$$

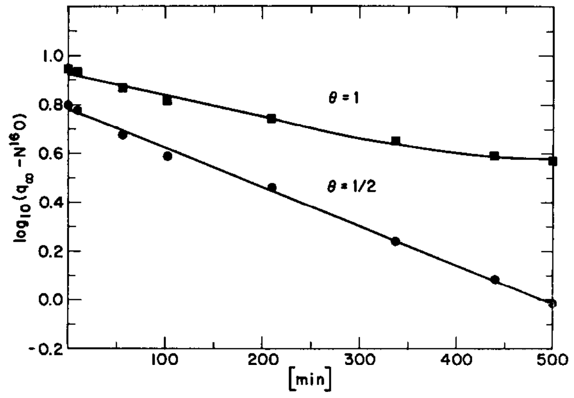

FIG. 6. First order plots for NO exchange on SC at 165.1°C (q in μmole).

The values of b and m depend on the number of exchangeable oxygen atoms in the solid. If it is assumed that this amount comprises a certain fixed fraction (or multiple) θ of one monolayer, v_m, then $b = \theta v_m + q_0$ (where q_0 is the $N^{16}O$ impurity in the gas phase at the beginning of the experiment) and $m = \theta v_m$, since the amount of ^{18}O in the solid at the beginning is negligible. Inserting these quantities and solving for q_∞ yields

$$q_\infty = a(\theta v_m + q_0)/(a + \theta v_m). \qquad (5)$$

Conversely, Eq. (5) can be used to estimate the extent of surface oxygen participation in the exchange. If it is assumed, in a first approximation, that q_∞ is given by the amount of $N^{16}O$ in the gas phase at termination of the exchange, after a long time, the amount of exchangeable oxygen is

$$\theta v_m = a(q_\infty - q_0)/(a - q_\infty). \qquad (6)$$

The experimentally observed limits of θ, as calculated from the appearance of $N^{16}O$, are $\theta = 0.83$ for the PC sample at 387°C, and $\theta = 0.71$ in the case of the SC sample at 165°C.

Equation (4) describes the exchange process by first order kinetics and can be written in an integrated form as

$$\log_{10}[(q_\infty - q)/q_\infty] = At. \qquad (7)$$

This equation is quite appropriate for the description of gas-phase exchanges (*17*), but requires energetic equivalence of the exchangeable surface species, when applied to solids (*2*, *4*, *18*). Adsorption sites on actual solid surfaces are usually not equivalent. In particular NO adsorption on polycrystalline NiO indicates a distribution of site energies, as the isotherms are of the Freundlich type (*14*). The single crystals, which expose only one crystal face, are expected to provide a more uniform surface.

It is instructive to compare the NiO–NO exchange kinetics with Eq. (7), which is based on the assumption of a uniform surface. Two values of q_∞ (θ), derived from Eq. (5), are considered for plotting $\log_{10}(q_\infty - q)$ vs time. The first choice is simply a monolayer of exchangeable oxygen ($\theta = 1$). However, a monolayer of the (111) NiO surface which consists of O (or Ni) ions alone is highly questionable from an energetic viewpoint. Kummer and Yao (*19*) have pointed out that this crystal face is more likely equally populated by anions and cations, corresponding to $\theta = 0.5$. The first order plot for the SC crystals at 165°C, shown in Fig. 6, yields a straight line in the case of $\theta = 0.5$. In contrast, the corresponding plot for $\theta = 1$ shows some curvature. These plots support the notion that (a) the single crystals have relatively uniform site energies and (b) the model of a half-populated surface represents the availability of exchangeable oxygen at this temperature better than does the monolayer. Corresponding plots for the PC sample at 293°C (Fig. 7) show a pronounced curvature, especially in the beginning of the exchange. This indicates that first order

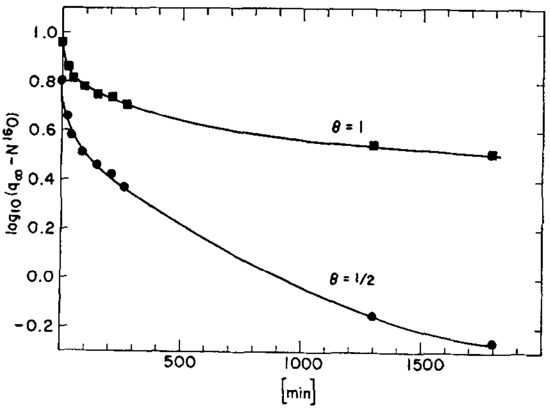

FIG. 7. First order plots for NO exchange on PC at 293.4°C (q in μmole).

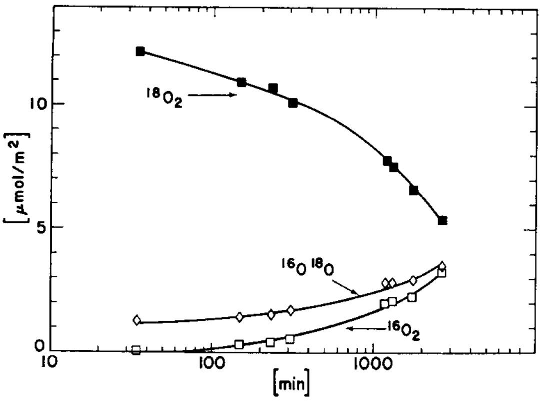

FIG. 8. Oxygen isotopes in the gas phase during NiO-O_2 exchange over PC at 416.7°C.

kinetics cannot describe the oxygen exchange on this surface, as one might expect in the case of a nonuniform distribution of surface sites. Atkinson *et al.* (*20*) have shown that the kinetics of heterogeneous isotope exchange reactions can be approximated by the Elovich equation, which is also suggested by the linearity of the plots in Fig. 2. However, we did not attempt to fit the data of the PC NiO quantitatively by the Elovich equation model (*20*).

NiO–O_2 Exchange

The exchange between molecular oxygen and the surface of an oxide is more complicated than that of NO with the same surface, as there are three isotopes $^{18}O_2$, $^{16}O^{18}O$ and $^{16}O_2$ to be considered instead of two. The oxygen exchange of the PC sample at 416°C, after the pretreatment described above, is given by Fig. 8, where the amounts of the three oxygen isotopes in the gas phase are plotted on a logarithmic time scale. Higher temperatures are required for the NiO–O_2 than for the NiO–NO exchange. The material balance indicates that 18% of the initial 14.7 μmole of O_2 has been adsorbed on the solid surface or incorporated into the bulk by the end of the experiment. The NiO–O_2 exchange at 297°C on the SC sample, subjected to the same pretreatment as the PC material, is illustrated by Fig. 9. The surfaces of the PC and the SC sample show a similar course of exchange (Figs. 8 and 9), in contradistinction to the NiO–NO exchange (Figs. 2 and 3). The material balance shows that only 10% of O_2 has been lost to the solid at this lower temperature. This fact indicates that NiO picks up more oxygen from the gas phase with increasing temperature (*21*).

The initial exchange rates, normalized to 300°C and 1 Torr, are incorporated into Table 2 for a comparison with the results of other investigators. There exists a large spread in exchange rates (10^{13}–10^{17}), activation energies (15–45 kcal/mole) and reaction orders (0–0.5). If the two highest exchange rates in Table 2 (Refs. (*10*) and (*11*)) are disregarded, the exchange rate of the SC sample is in agreement with the remaining rates within a factor of 5. The PC sample yields a rather low exchange rate, probably because of a higher impurity level.

Because of two exchangeable atoms in each oxygen molecule several exchange modes are possible. In contrast to NO, O_2 can undergo molecular exchange without O–O bond scission, as well as atomic exchange. Moreover homomolecular exchange between two oxygen molecules on the surface masks the exchange modes of the surface oxygen. Let us consider the isotope distribution in the gas phase as a function of time. The ratio

$$r = (^{16}O^{18}O)^2/[(^{16}O_2)\cdot(^{18}O_2)] \qquad (8)$$

is suited as a measure for this distribution,

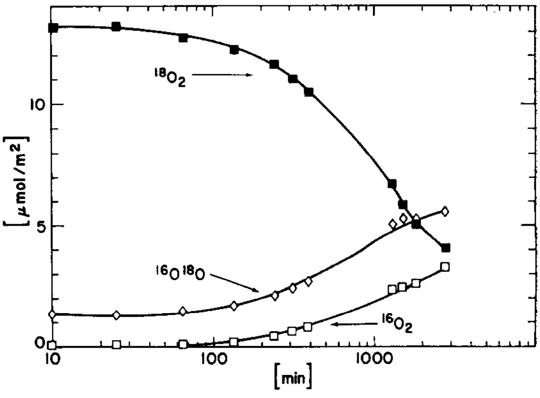

FIG. 9. Oxygen isotopes in the gas phase during NiO-O_2 exchange over SC at 297.4°C.

TABLE 3
Distribution of Oxygen Isotopes in the Gas Phase (Data of Fig. 9)

Time (min.)	Oxygen percentages $^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	$\frac{(^{16}O^{18}O)^2}{(^{16}O_2)\cdot(^{18}O_2)}$
0	0	8.4	91.6	∞
10	0.1	8.9	90.9	8.7
25	0.1	9.2	90.7	9.3
65	0.4	10.2	89.4	2.9
135	1.1	12.0	86.8	1.5
240	3.0	14.9	82.1	0.9
310	4.4	17.2	78.4	0.9
390	5.5	19.3	75.1	0.9
1275	16.9	35.2	47.9	1.5
1290	16.9	36.1	47.0	1.6
1500	18.3	38.4	43.3	1.9
1800	20.3	40.6	39.1	2.0
2725	26.1	42.7	31.2	2.2
2750	25.9	43.0	31.1	2.3

since at equilibrium it has a fixed value of 4. The numerical data of the run in Fig. 9, given in Table 3, show that initially $r = \infty$ due to the absence of $^{16}O_2$. In the first stage of the exchange the ratio drops rapidly past the equilibrium ratio of 4. This decrease indicates a process which leads to a relatively rapid appearance of $^{16}O_2$ in the gas phase and is faster than any of the processes that tend to equilibrate the gas phase. Equilibration between the gas molecules occurs via homomolecular exchange, without the participation of surface oxygen,

$$^{16}O_2 + {}^{18}O_2 = 2\,{}^{16}O^{18}O, \qquad (9)$$

and where only one oxygen atom in the surface participates at a time, such as

$$^{18}O_2 + (^{16}O)_s = {}^{16}O^{18}O + (^{18}O)_s. \qquad (10)$$

Processes that will cause initially an excess of $^{16}O_2$ in the gas phase may involve the exchange of oxygen molecules, chemisorbed on the surface

$$^{18}O_2 + (^{16}O_2)_{ads} = {}^{16}O_2 + (^{18}O_2)_{ads}, \qquad (11)$$

or simultaneous, concerted exchange of two oxide ions

$$^{18}O_2 + 2(^{16}O)_s = {}^{16}O_2 + 2(^{18}O)_s. \qquad (12)$$

We tend to believe that process (11) outweighs process (12). As the surface becomes exhausted of $^{16}O_2$ molecules, the isotope ratio r resumes an upward trend. As will be discussed below, N_2O also tends to dislodge oxygen from the surface; such a phenomenon was, however, not observed when NO was contacted with NiO.

Nováková (*16*) has shown that the consideration of several possible exchange modes, taking into account a uniform surface only, leads to a rather complex expression of the exchange kinetics. The predominant exchange occurs on single sites, in accordance with Eq. (10). Winter (*3*) and Boreskov (*4*) agree that a second important exchange mode on NiO proceeds via oxygen pairs (Eq. (11) or (12)). Winter estimates from his data on NiO that this second mechanism accounts for about 20% of the total oxygen exchange. First order plots based on Eq. (7), which take into account the total amount of exchanged oxygen, were found not to be linear for both the PC and the SC samples. This is not surprising in view of the complex exchange process. The existence of a minimum in the isotope ratio below the equilibrium ratio has been discussed in detail by Klier *et al.* (*18*).

It is interesting to note that especially at higher temperatures more than one monolayer of oxygen atoms can participate in the NiO–O_2 exchange. Experimentally observed limits of the exchange, derived in analogy to Eq. (6), are $\theta = 1.48$ (PC at 551°C) and $\theta = 1.84$ (SC at 396°C). Values $\theta > 1$ can be attributed, in part, to the adsorbed oxygen discussed above. However, most of the excess is probably due to oxygen from subsurface layers.

NiO–N_2O Exchange

When $N_2{}^{18}O$ was contacted with the PC sample in the temperature range from 400–500°C, the only reaction that took place, was the decomposition of the nitrous oxide into N_2 and O_2 with the incorporation of some oxygen into the solid. The ratio $N_2{}^{18}O/(N_2O)_{total}$ in the gas phase remained constant and equal to that of the initial mixture throughout the experiment, until all of the N_2O had disappeared. The isotopic composition of the oxygen which appeared in the gas phase indicated that in the beginning a large percentage of the oxygen (>70%) was released as $^{16}O_2$. This observation can be explained by the displacement of adsorbed oxygen molecules from the surface by N_2O molecules, similar to that observed in the NiO–O_2 exchange. As the contact time between N_2O and NiO was increased, the equilibrium ratio (cf. Eq. (8)) was gradually approached, due to the exchange process between the product oxygen molecules and the NiO surface.

To discern whether an N_2O molecule can truly exchange its oxygen atom, it became necessary to employ a surface of NiO with a more labile oxygen in the surface, and to carry out the experiment at a lower temperature, to decrease the rate of N_2O decomposition which otherwise overwhelms the exchange. Indeed, when using the SC sample at 310°C the ratio of the nitrous oxide isotopes changed, albeit very slowly, as shown in Fig. 10, indicating that the exchange process takes place. Winter (*2*) has tried to ascertain the occurrence of the N_2O exchange with NiO–Cr_2O_3, apparently without success.

CONCLUSIONS

It has been shown that NiO exchanges its surface oxygen as easily as does Fe_2O_3. Apparently surface groups formed upon contact with NO serve as intermediates to accomplish the exchange without dissociative chemisorption of NO. Symmetrical surface ions, which can be described as NO_2^{2-}, have been recently identified on oxide surfaces exposed to NO, both by ESR (*22–24*) and ir spectroscopy (*25, 26*). A surface covered by such groups could dynamically exchange NO with the gas phase. The NO disengaged from the surface contains, more or less randomly, oxygen atoms derived from the adsorbed molecules and from the surface. The observed exchange and its extent suggest that the prevalent mode of NO adsorption on metal oxides may be, indeed, the doubly coordinated NO molecule, which attaches its N atom to both a metal and an oxygen ion in the surface. This view has been recently advanced by several investigators (*23, 24, 26*). It is to be expected that other oxides besides Fe_2O_3 (*1*) and NiO will behave in a similar manner.

The kinetics of the NiO–NO exchange on single crystals of high purity, which expose only one crystal face, are well represented by an equation based on two assumptions: (a) energetic equivalence of surface exchange sites and (b) confinement of the reservoir of uniformly exchangeable surface oxygen to half a monolayer (or more correctly, one monolayer equally populated by Ni and O ions).

A less pure and polycrystalline NiO sample did not follow the same exchange behavior, and a different kinetic model based on the Elovich equation has to be applied (*20*), but has not been pursued here. The differences in the exchangeability

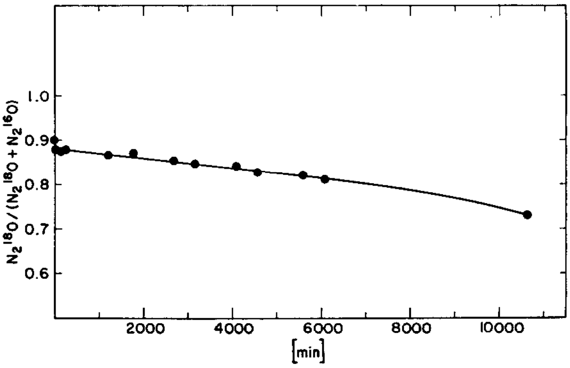

FIG. 10. Ratio of N_2O isotopes during contact of $N_2{}^{18}O$ with SC at 310°C.

of surface oxygen in NiO are due more to heterogeneities introduced by impurities than by the presence of different crystal faces.

The energy barriers, as expressed by the apparent activation energies, or by the temperatures required for the onset of the exchange, are substantially higher in the case of the NiO–O_2 exchange as compared to the NiO–NO exchange. The requirement of dissociative chemisorption of the O_2 molecule for the major exchange path is sufficient to explain this observation.

The oxygen exchange between NiO and N_2O is very slow and complicated by the competing N_2O decomposition. On the other hand, the observable exchange indicates that the formation of a surface complex takes place, where the N_2O molecule is coordinated to a surface oxide ion through the nitrogen end, but probably to a very small extent only.

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