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Behavior of Oxygen Species on the Nickel Oxide Catalyst Surface

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The ^{18}O-oxidation of carbon monoxide was studied on nickel oxide catalysts, and the oxygen exchangeability with the oxide during the reaction was determined. The activities of three oxide samples, obtained under different preparation conditions, were compared. The samples were prepared at 350, 600, and 850°C; they are denoted as NiO-I, NiO-II, and NiO-III respectively. In the case of NiO-I, two kinds of oxygen species, weakly and strongly bound to the surface, were observed. Above 120°C, not only weakly but also strongly bound surface oxygen become reactive; however, the binding energy distribution was quite broad. Similar observations were made in the case of NiO-II, with a similar change above 170°C and with a sharp energy distribution. In contrast, for NiO-III, only a small percentage of the monolayer of the surface oxygen became active and exchangeable below 200°C, but above 250°C about three layers became activated. Models are proposed for the surface state of these oxides on the basis of the behavior of the surface oxygen.

A number of studies have been devoted to the investigation of the oxidation of carbon monoxide over nickel oxide catalysts, but the proposed rate expressions and reaction mechanisms differ from author to author.[1–9] This very fact suggests that the surface structure and properties of the nickel oxide used differ intricately with its biography.

Recently, Uchijima *et al.*[10] successfully measured the amount of "surface excess oxygen" and its oxidation power distribution, and showed that the surface state of nickel oxide varied delicately, depending upon the preparation conditions, especially the sintering temperature of the oxide. Such conclusions were also reported by Dere'n *et al.*[11] However, a main problem still remains whether or not the surface excess oxygen is an effective parameter in the discussion of the mechanism.

In order to examine the behavior of the surface oxygen under the conditions of the working state, the oxidation of carbon monoxide was investigated in the present study by the use of ^{18}O-tracer on nickel oxides, which had been prepared under three different preparation conditions.

Experimental

Table 1. Preparation conditions and some characteristics of the NiO samples

Catalyst	Preparation conditions Temperature (°C)	Decomposition time (hr)	Sintering time (hr)	BET surface area (m^2/g)	Color
NiO-I	350	3	15	64.0	Black
NiO-II	600	3	15	4.1	Grayish Green
NiO-III	850	3	15	0.9	Green

Material. The NiO catalysts were prepared by the decomposition of $NiCO_3$, followed by sintering. $NiCO_3$ precipitated by mixing an aqueous solution of $Ni(NO_3)_2$ and $(NH_4)_2CO_3$ (both special grade; Wako Pure Chem. Ind. Co.) was completely washed, filtered and dried in a vacuum desiccator containing $CaCl_2$. The preparation conditions, the B.E.T surface area, and colors of the catalysts are summarized in Table I. The B.E.T. surface areas were determined from the adsorption of nitrogen at 77°K.

Carbon monoxide was obtained by the reaction of formic acid and conc. sulfuric acid. Heavy oxygen (4.8 atom% ^{18}O) was obtained by the electrolysis of heavy water containing ^{18}O. Both gases were purified by the usual methods and were found to be mass-spectrometrically pure.

Reaction Apparatus and Procedure. The reaction was carried out in a thermo-cyclic reaction vessel (265 cc), as is shown in Fig. 1. The amount of the catalyst used was 0.5 g in the cases of NiO–I and NiO–II and 2.0 g in the case of NiO–III. After the heat treatment at 300°C in a vacuum (10^{-5} Torr) for 2 hr, 32—36 mmHg of the reaction gas ($CO:O_2=2:1$) was introduced into the reaction vessel. The change in the total pressure was measured with a mercury manometer, and the change in the composition

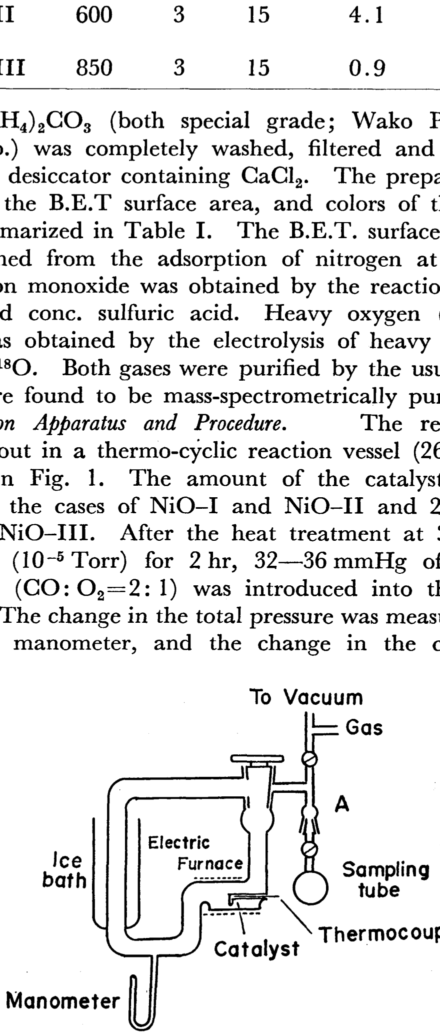

Fig. 1. Thermo-cyclic type reaction vessel.

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of reacting gases and their ^{18}O-concentration, with a mass spectrometer.

The errors of the ^{18}O-concentration were within 0.02—0.1 atom%. The temperature was kept constant within ± 1.0°C.

Results

Carbon Monoxide Oxidation on NiO-I and the Distribution of ^{18}O among the Components during the Reaction. The reaction was carried out in the temperature range from 50° to 350°C, and arrived at equilibrium in all runs except the run at 50°C. The ^{18}O-concentration in unreacted oxygen remained almost the same at its initial value (4.8 atom% ^{18}O), and that in unreacted carbon monoxide gave a constant value equal to the natural abundance or a slight increment during the reaction. On the other hand, the ^{18}O-concentration in the produced CO_2 varied with the time, depending upon the reaction temperature, as is shown in Table 2. From the findings that the ^{18}O-concentrations in oxygen and carbon monoxide remained the same at their initial values, while the $C^{16}O^{18}$ O% in carbon dioxide always changed with a value lower than the ^{18}O atom% in oxygen during the reaction, it is clear that oxygen species in the catalyst, NiO-I take part in the catalytic oxidation.

TABLE 2. CHANGE IN $C^{16}O^{18}O$% IN PRODUCED CO_2 DURING THE COURSE OF REACTION ON NiO-I, 0.5 g

Reaction temperature (°C)	Time (min) 2	5	10	15	60
50	—	4.47	4.48	4.58	4.44
80	—	4.71	4.05	4.13	3.82
100	—	3.59	3.71	3.66	3.52
120	—	3.30	3.50	3.60	3.45
150	—	3.33	3.46	3.40	3.38
200	—	3.06	3.25	3.13	3.13
250	—	2.70	2.97	2.82	2.73
300	1.89	—	2.42	2.45	2.46
350	—	2.14	2.04	2.01	1.73

Considering the material balance of ^{18}O during the oxidation, the relation for obtaining the amount of exchangeable or reactive oxygen in the catalyst can be represented by Eq. (1):

$$(\alpha-\beta)n_g = (\beta/2)n_s \qquad (1)$$

where the notations are:

α: ^{18}O atom% in gaseous oxygen
β: $C^{16}O^{18}$ O% in carbon dioxide
n_g: number of molecules in the produced carbon dioxide
n_s: number of exchangeable or reactive oxygen atoms in the catalyst.

The left-hand side of Eq. (1) indicates the number of ^{18}O atoms which disappear from the gaseous phase, and the right-hand side, the number of ^{18}O atoms captured by the catalyst, on the assumption of an isotopic equilibrium between the ^{18}O-concentrations in the produced carbon dioxide and that in the catalyst. Then, the number of the exchangeable or reactive oxygen atoms, n_s, is given by Eq. (2):

$$n_s = 2(\alpha-\beta)n_g/\beta \qquad (2)$$

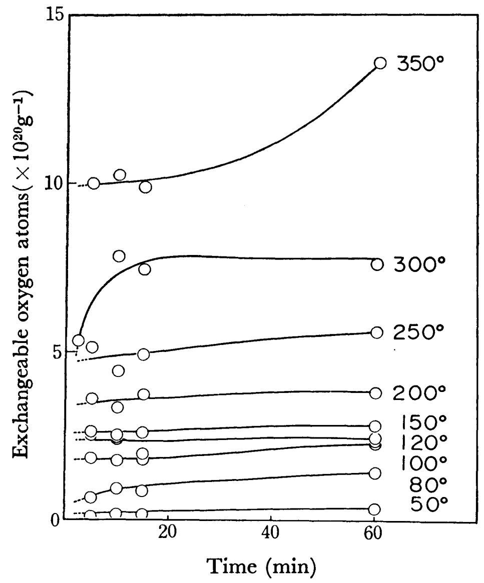

Fig. 2. Temperature dependency of exchangeable oxygen atoms of the surface (n_s) during the oxidation on NiO–I.

The change in n_s with the time, obtained for NiO-I by Eq. (2), are compared in Fig. 2. The figure shows that the n_s remained practically the same after 15 min in all temperatures except at 350°C, though the magnitude depends upon the reaction temperature. This shows that the exchange process of oxygen between carbon dioxide and the catalyst (NiO-I) is very fast. The assumption of the exchange equilibrium, therefore, may be unnecessary at 60 minutes in all runs except that at 350°C.

Carbon Monoxide Oxidation on NiO-II and the Distribution of ^{18}O among the Components during the Reaction. The reaction was carried out in the temperature range from 100° to 400°C, and the reaction equilibrium was practically reached within 10—15 min, except for the run at 100°C. The ^{18}O-concentrations in unreacted O_2 and CO almost remained at their initial values, as in the case of NiO-I. The ^{18}O-concentration in the produced CO_2 changed with the time, as is shown in Table 3.

The numbers of the exchangeable or reactive oxygen atoms, obtained from the Eq. (2), are given in Fig. 3. The n_s in NiO-II is about ten times smaller than that

TABLE 3. CHANGE IN $C^{16}O^{18}O$% IN PRODUCED CO_2 DURING THE COURSE OF REACTION ON NiO-II, 0.5 g

Reaction temperature (°C)	Time (min) 2	5	10	15	60
100	4.60	4.67	4.66	4.65	4.71
150	4.75	4.75	4.70	4.70	4.76
170	4.65	4.62	4.62	—	4.67
190	4.61	4.64	4.63	—	4.67
200	4.70	4.72	4.66	—	4.51
300	4.56	4.59	4.55	4.45	4.27
400	4.09	4.20	4.18	4.20	4.00

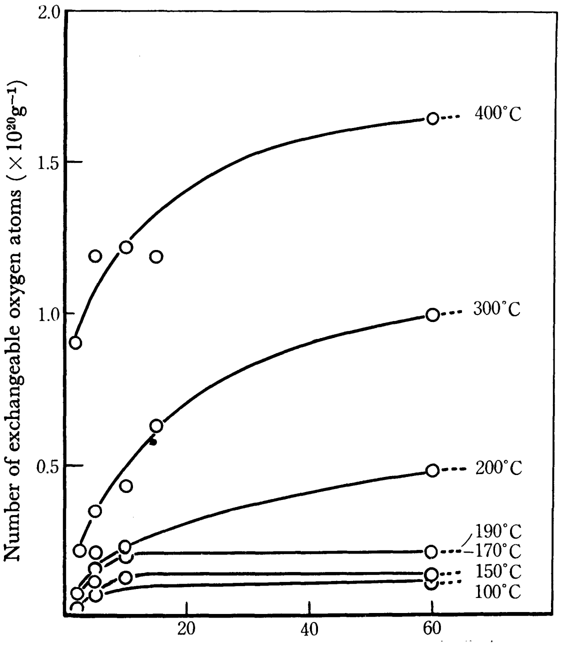

Fig. 3. Temperature dependency of exchangeable oxygen atoms of the surface (n_s) during the oxidation on NiO–II.

in NiO-I; therefore, the errors are estimated to be more or less large. However, it can be observed that the values of n_s remained the same after 10—15 min, at least at temperatures below 190°C. In the case of NiO-II, the exchange equilibrium is not established even after one hour above 200°C, which is lower than in the case of NiO-I.

Carbon monoxide Oxidation on NiO-III and the Distribution of ^{18}O *among the Components during the Reaction.* The reaction was carried out in the temperature range from 200° to 400°C. The reaction equilibrium was reached within 10—15 minutes in all runs except that at 200°C. The ^{18}O-concentrations in unreacted oxygen and carbon monoxide remained constant at all runs during the course of the reaction, as in the cases of NiO-I and NiO-II. On the other hand, the $C^{16}O^{18}O$% in the CO_2 produced varied with the time, as is shown in Table 4.

The numbers of the exchangeable or reactive oxygen atom, n_s, obtained from Eq. (2), are recorded in Fig. 4. The n_s values show that, in the runs above 280°C, the isotopic equilibrium between CO_2 and the catalyst is still not established even after 60 minutes.

TABLE 4. CHANGE IN $C^{16}O^{18}O$% IN PRODUCED CO_2 DURING THE COURSE OF REACTION ON NiO-III, 2.0 g

Reaction temperature (°C)	Time (min) 2	5	10	15	60
200	4.4	—	—	4.76	4.71
250	4.55	—	4.66	4.78	4.71
280[a]	4.67	4.68	4.65	—	4.56
300	4.51	4.68	—	4.69	4.37
330[b]	4.55	4.66	4.68	4.68	4.57
350	4.52	4.60	4.49	4.37	4.21
400	4.55[c]	4.55[d]	4.35	4.41	4.20

a) 1.5 g b) 1.0 g c) 3 min d) 6 min

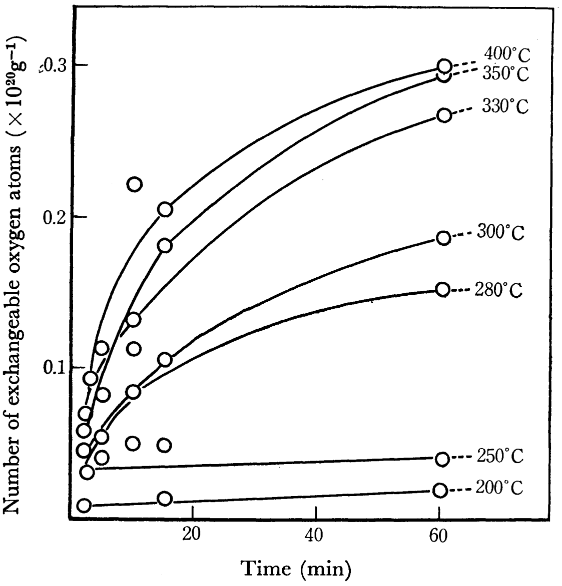

Fig. 4. Temperature dependency of exchangeable oxygen atoms of the surface (n_s) during the oxidation on NiO–III.

Discussion

The crystal structure of nickel oxide belongs to that of the NaCl type. If it is assumed, for the sake of convenience, that the exposed surface consists of only the (100) plane, the number of the exchangeable or reactive atoms, n_s, can be easily transformed into the surface fraction of the oxygen atom, θ (n_s). The surface fractions, θ (n_s), obtained on the assumption from the n_s values at 60 min shown in Figs. 2, 3, and 4 are shown in Figs. 5, 6, and 7 respectively.

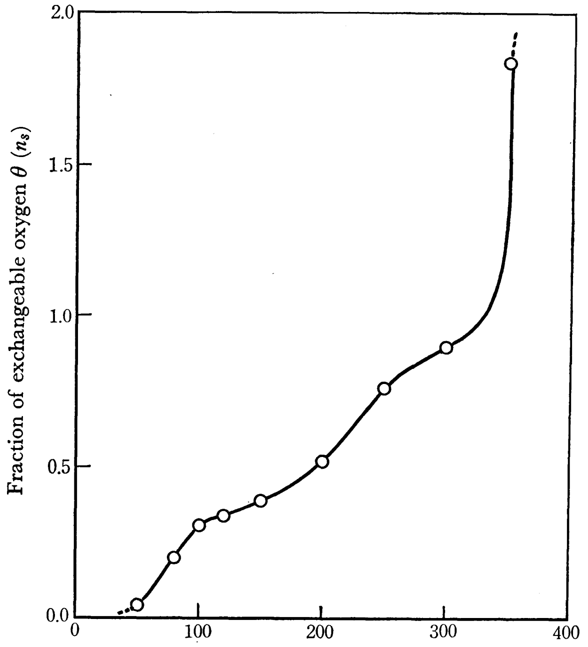

Fig. 5. Fraction of the exchangeable oxygen to the monolayer *versus* reaction temperature on NiO–I.

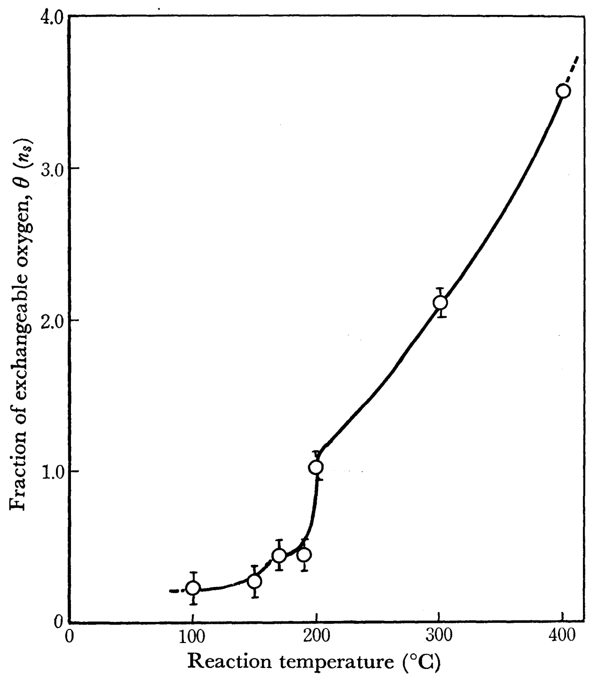

Fig. 6. Fraction of the exchangeable oxygen to the monolayer *versus* reaction temperature on NiO–II.

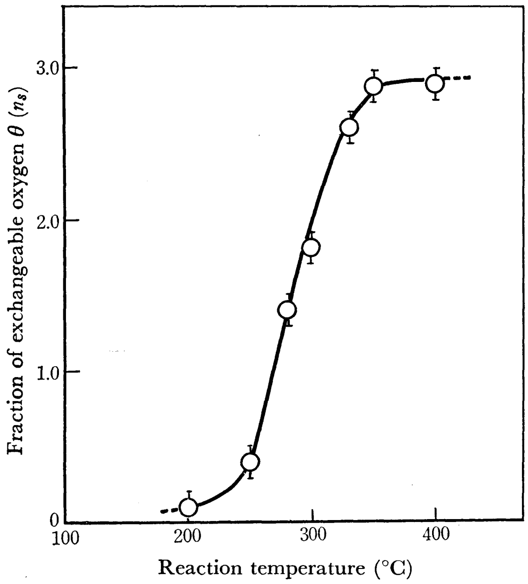

Fig. 7. Fraction of the exchangeable oxygen to the monolayer *versus* reaction temperature on NiO–III.

NiO-I (Fig. 5) shows clear changes in the exchangeability of the oxide at about 120 and 300°C. Oxygen species, which are exchangeable with carbon dioxide or which take part in the reaction below 120°C, correspond to about 30% of the surface, while those in the temperature range between 120 and 300°C correspond to about 60%. By raising the reaction temperatute to above 300°C, the oxygen species in the second layer or below also become exchangeable.

NiO-II (Fig. 6), though the errors are estimated to be more or less large, shows a clear change in the exchangeability at two temperatures, *i.e.*, between 150 and 170°C and between 190 and 200°C. About 40% of the surface is covered with the oxygen species, which can exchange with carbon dioxide or take part in the reaction below 170°C, while about 60% of the remaining surface is covered with the oxygen species, which can participate in the reaction at a temperatute between 170 and 200°C. Since Fig. 6 shows an abrupt change in the exchangeability in the higher-temperature region within a narrower temperature range in comparison with Fig. 5, the surface of NiO-II seems to have less heterogeneity than that of NiO-I.

In the case of NiO-III, the exchangeability increases rapidly and monotonously above 250°C, reaching a constant value at 350° and 400°C, indicating that the amount of the exchangeable or reactive oxygen corresponds practically to the three layers near the surface, that is, the binding state of the oxygen of the first three layers is homogeneous; moreover, the state in the three layers near the surface and that below the layers are clearly different in exchangeability from the above layers.

From the above discussion, the following surface models can be proposed for nickel oxide catalysts:

(i) NiO-I: The surface oxygen is roughly classified in two groups based on the difference in binding energy. About 30% of the surface oxygen is weakly-bound oxygen (W-site), and about 60%, strongly-bound oxygen (S-site). The former becomes reactive even below 120°C, and the latter, in the temperature range between 120 and 300°C, but the distribution of the binding energy is widespread.

(ii) NiO-II: The surface oxygen is composed of about 40% weakly-bound oxygen (W-site) and about 60% strongly-bound oxygen (S-site). The former becomes reactive below 170°C, and the latter, in the temperature range between 170 and 200°C, and the distribution of the binding energy is not so widespread.

(iii) NiO-III: The three layers near the surface are very homogeneous, and the layers below them are clearly different in exchangeability.

Dere'n *et al.*[11] suggested that "excess oxygen," *i.e.*, the ionosorbed oxygens of NiO, are almost entirely concentrated on the surface and are completely removed by evacuation for several minutes at 400°C. According to their suggestion, the surface oxygen which is not in the form of the surface-excess oxygen has become the object of the present research, because in our research the surface-excess oxygen can be removed by pretreatment. From this viewpoint, the results of other authors obtained by kinetic studies, desorption studies of oxygen and carbon dioxide, ^{18}O-exchange studies, and so on will be compared with ours and examined in connection with the above surface model.

Kondo *et al.*[1] observed the desorption of carbon dioxide with the elevation of the temperature on NiO, which seems to have nearly the same properties as NiO-I, because it was prepared by the decomposition and sintering of $NiCO_3$ at 350°C for 24 hr. They found the existence of two types of adsorption sites on the surface; which correspond to the maxima of the desorption curve at 80 (weak adsorption site) and at 300°C (strong adsorption site). Moreover, they measured the rate of the CO-oxidation on the NiO, poisoned by carbon dioxide, and suggested that the strongly-adsorbed carbon dioxide exists on the site of weakly-bound oxygen of the surface, while, conversely, the weakly-adsrobed carbon dioxide exists on that of strongly-bound oxygen. They concluded that the oxidation rate was controlled by the process on the former site below 110°C and by that on the latter site above this temperature.

The temperature, 120°C, above which the S-site also becomes reactive on NiO-I corresponds fairly well to their transition temperature. However, it is difficult to understand their conclusion that, at lower temperatures, the oxidation rate is controlled by the process on the site of the strong adsroption of carbon dioxide, because the carbon dioxide produced cannot be desorbed from the site at such a temperature, but can be desorbed only at around 300°C. The present results, that the values of $C^{16}O^{18}$ O% increase with the time in the initial stage, suggest that the CO-oxidation is initiated by the extraction of the surface oxygen with carbon monoxide; below 120°C, only the W-site takes part in the oxidation, while above that temperature the W-site and also the S-site in accordance with the reaction temperature take part in the oxidation. Since the ^{18}O-concentration in both carbon monoxide and oxygen gases remained unchanged during the reaction, the stoichiometric change in the reacting gases was observed, and no poisoning effect was indicated, so it is clearly shown by Fig. 8 that Step I or Step II is a very slow process. However, it is not yet clear whether Step I or Step II corresponds to the rate-controlling step below and above the transition temperature.

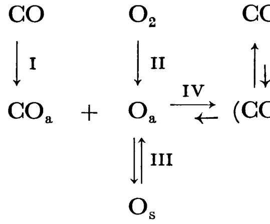

Fig. 8. Schematic representation of carbon-monoxide oxidation

Kondo *et al.*[1)] carried out the same experiment on NiO, which seems to have nearly the same properties as NiO-II; *i.e.*, their oxide was prepared by the decomposition and sintering of $NiCO_3$ at 700°C for 4 hr. The peaks of the CO_2 desorption curve shifted to a higher temperature and the transition temperature of the CO-oxidation became 160°C. Therefore they drew the same conclusion as above. This transition temperature may correspond to the temperature, 170°C, above which the S-site on NiO-II also becomes reactive, but their mechanism has been found to be inconsistent with the present one, as will be discussed below. Parravano[2)] investigated the kinetics of carbon-monoxide oxidation on NiO, which seems to have nearly the same properties as NiO-II; *i.e.*, their oxide was prepared by firing $NiCO_3$ at 640°C for 3 hr. He showed that the rate expression between 106 and 174°C was different from that between 205 and 222°C, while the Elovich equation holds in both temperature ranges at the initial stage. He concluded that, at the initial stage, Eq. (3) controlled the reaction rate. At the stationary state of the reaction, Eq. (3) became the rate-determining step in the lower temperature range, while Eq. (4) was that step in the higher:

$$\mathrm{CO} + \mathrm{O(s)} \longrightarrow \mathrm{CO_2} + \mathrm{(s)} \qquad (3)$$

$$\frac{1}{2}\mathrm{O_2} + \mathrm{(s)} \longrightarrow \mathrm{O(s)} \qquad (4)$$

The finding for NiO-II that the values of $C^{16}O^{18}$ O% tend to increase rapidly at the initial stage is consistent with Parravano's conclusion that the reaction is initiated by the extraction of surface oxygen with carbon monoxide. Based on the surface model of NiO-II, it can be expected that the oxidation rate in the temperature range between 174 and 205°C, where Parravano did not give any rate expression, is controlled by a different process. Up to 170°C, only the oxygen in the W-site would take part in the reaction, while in the range from 170 to 200°C not only the oxygen on the W-site but also that on the S-site would take part, according to the temperature. Since the ^{18}O-concentrations of O_2 and CO remained the same during the reaction, Step I or Step II in Fig. 8 must be very slow.

Winter[3)] investigated the CO-oxidation in the temperature range between 40 and 211°C on $Ni^{18}O$, which was obtained by means of the ^{18}O-exchange between $C^{18}O_2$ and NiO, which seems to have nearly the same properties as NiO-III; *i.e.*, it was prepared by the decomposition of $NiCO_3$ at 870°C for 24 hr. The result indicated that only 2.3% of the surface oxygen takes part in the oxidation. Recently, Gay[12)] measured the desorption spectra of adsorbed oxygen on NiO, prepared by the decomposition of $NiCO_3$ at 850°C for 9 hr. He indicated that only a small percentage of surface oxygen became desorbable by the elevation of the temperature to 750°C. The results of both Winter and Gay suggest that only a small percentage of the surface oxygen is active on NiO prepared at the higher temperature. The present results for NiO-III show that the surface oxygen, activated below 200°C in the oxidation, is less than 10%, but otherwise, above 250°C, about three layers of the surface are activated to the same degree. Therefore, it might be expected that the reaction mechanisms in the temperature ranges below 200 and above 250°C are different.

The above discussions were done without considering the surface excess oxygen or ionosorbed oxygen, but the contributions of these species cannot be ruled out, especially at room temperature. Not only CO-oxidation but also interactions among the adsorbed species, O_2, CO, and CO_2, on NiO have been investigated at such low temperatures by several authors.[13–18)] For

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instance, Teichner,[13] Garner,[14] and Stone[15] measured the heat of adsorption of CO, O_2, and CO_2, and their heat of reactions on the catalyst. They pointed out the existence of a CO_3-complex, and also suggested that the oxidation reaction could proceed through the path of the formation of the complex on NiO, though they used very different catalysts. Teichner[16] and Eischens[18] have confirmed the existence of the CO_3-complex by measuring the IR spectra of the reacting system. From these results, it can be expected that the site of excess oxygen plays an important role in the formation of the CO_3-complex and in the course of the oxidation reaction at low temperatures.

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