BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2257—2263 (1968)

Changes in Catalytic Activity and Surface Properties of Nickel Oxide with Gamma-Irradiation

Toshiro YAMASHINA, Takaaki NAGAMATSUYA[*1] and Masakatsu SANO

Faculty of Engineering, Hokkaido University, Sapporo

(Received January 27, 1968)

The nature of the active sites of nickel oxide has been studied by changing surface properties by means of γ-irradiation technique. Using powdered nickel oxide catalyst, catalytic activities, surface excess oxygen contents, electrical conductivity changes during thermal desorption of gases, and reactivities of the sample with CO_2, CO and H_2 were compared as a function of γ-ray dose of preirradiation. It has been found that the catalytic activity, the excess oxygen content and the conductivity change with the increase in the irradiation dose, and the change is remarkable when a total dose is greater than 1×10^8R. The catalytic activity for the decomposition of H_2O_2 was observed to increase, while that for the decomposition of i-C_3H_7OH vapor was observed to decrease with the irradiation dose. Measurements on the desorption of excess oxygen and the adsorption of CO_2 simultaneously with electrical conductivity have indicated that the adsorbed state of surface oxygen may be changed into a strong form by the irradiation, as $O^-_{(ad)} \rightsquigarrow O^{2-}_{(ad)}$. Discussions have been made on the correlation between the catalytic sites and surface properties of the irradiated nickel oxide.

Many studies have been made on the surface chemistry of nickel oxide as well as that of other transition-metal oxides, and particular interest is shown in the surface heterogeneity of the oxides. The surface heterogeneity of powdered nickel oxide has been investigated by various methods, including the determination of the distribution of surface excess oxygen,(1) isotopic exchange reaction technique,(2,3) electrical conductivity measurement during adsorption or desorption,(4) deactivation with CO_2 adsorption(5,6) and so on. However, there has been discrepancy among the results of

---

[*1] Present address: Japan Atomic Energy Institute, Ooarai, Ibaragi.

1) H. Gossel, *Z. Elektrochem.*, **65**, 98 (1961).

2) G. K. Boreskov, "Advances in Catalysis," Vol. 15, ed. by D. D. Eley, H. Pines and P. B. Weisz, Academic Press, New York (1965), p. 285.

3) K. Klier and M. Jiratova, Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1965 (1966), p. 763.

4) H. Saltsburg, D. P. Snowden and M. C. Garrison, *J. Phys. Chem.*, **68**, 3765 (1964).

5) G. Parravano and C. A. Demonicali, *J. Chem. Phys.*, **26**, 359 (1957).

6) J. Kondo, T. Uchijima and Y. Yoneda, This Bulletin, **40**, 1040 (1967).

different workers. This may be due to the difference in the method of sample preparation or experimental procedures. Accordingly, many unresolved problems on active sites and the chemical reactivity of nickel oxide surface have been remained.

The present investigation was undertaken to obtain some informations as to the state of surface excess oxygen in connection with active sites and the surface reactivity of nickel oxide. By means of irradiation the surface state of the oxide could be changed selectively. Thus the surface state has been examined from many viewpoints such as catalytic activity, the nature of excess oxygen, electrical conductivity and adsorption of gases as a function of irradiation dose of γ-rays.

Some results on the nature of the irradiated nickel oxide, *i. e.*, on the catalytic activity for the decomposition of H_2O_2 solution[7] and the reduction kinetics by H_2,[8] have been reported previously by the present authors. The purpose of this report is to describe some additional results of the previous study and some preliminary results obtained by using an apparatus connected with a quadrupole mass spectrometer for the adsorption and the desorption of CO_2 and i-C_3H_7OH.

Experimental

Materials. NiO sample was obtained by decomposing and firing CP grade nitrate in air at 500°C for 5 hr after a gentle evaporation of the dilute solution of the nitrate. The oxide product was reduced to a granular form (100—200 mesh). The BET surface area of this sample measured by nitrogen adsorption was 9—10 m²/g. Carbon monoxide (99.5%), carbon dioxide (99.95%) and isopropanol (spectro-grade) were obtained commercially. Hydrogen was purified by diffusing the crude gas through a palladium film.

Irradiation of sample was carried out in air at room temperature with Co-60 γ-rays, the intensity of which was 5.85×10^5 R/hr; total dose reached about 1×10^9 R.

Catalytic Activity. The catalytic activity of NiO was determined by using the decomposition of a 7.5% hydrogen peroxide solution as a model reaction. The rate of reaction was followed by measuring the volume of oxygen evolved per minute with the apparatus shown previously.[9] A 0.2 g catalyst sample was used for each run and the reaction temperature was 25—45°C. Before each run, the decomposition rate without catalyst was measured. Negligibly small amount of decomposition less than about 5% of that with catalyst was found to occur. The reproducibility in the determination of the catalytic activity was found to be better than 5%. The activity for the decomposition of i-C_3H_7OH was also measured by means of the apparatus described previously.[10]

Excess Oxygen Content and Electrical Conductivity Measurements. The quantity of excess oxygen in NiO was determined by an iodometric titration[9] and a gravimetric method with a vacuum microbalance. Chemical analysis by the iodometry was performed as follows: 0.5 g of KI, 50 *ml* of 35% HCl and 100 *ml* of H_2O were added to 0.5 g of catalyst sample and the sample was dissolved by heating gently. Under a nitrogen flow, the solution was cooled and allowed to stand in darkness, then the titration was made with a 0.01 N $Na_2S_2O_3$ solution as quickly as possible. Replicate titration experiments were made at least five times, the reproducibility in the determination being found to be better than 10%.

Electrical conductivity measurements were made by means of AC and DC potentiometric methods with a cell for powdered NiO shown in Fig. 1. An 1.0 g catalyst sample was inserted between two platinum plates (disc of 1 cm in diameter) and pressure of about 2 kg/cm² was applied with a steel spring. The closed end of a quartz tube containing the cell connected to a vacuum line was inserted into an electric furnace, then changes in the conductivity during the adsorption or the desorption of gases were measured. The resistivities of NiO were observed to be in the range from 10^5 to 10^8 Ω. Determinations both by the AC and DC methods gave nearly identical values of the resistance, and no polarization effect was observed in the measurement by the DC method. Accordingly, the following results in the present paper were obtained mainly by the DC method.

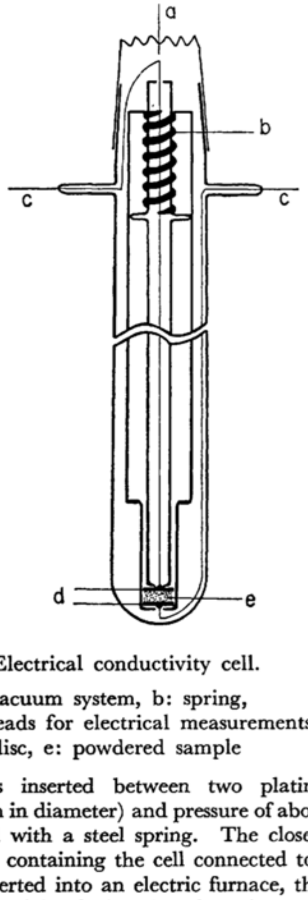


Fig. 1. Electrical conductivity cell.

a: to vacuum system, b: spring,
c: Pt leads for electrical measurements,
d: Pt disc, e: powdered sample

Adsorption and Desorption Measurements. Changes in the weight of catalyst samples during adsorption or desorption of gases were measured in an all

---

[7] T. Yamashina and M. Sano, This Bulletin, **38**, 1801 (1965).

[8] T. Yamashina and T. Nagamatsuya, *ibid.*, **38**, 507 (1965).

[9] T. Yamashina and M. Sano, *Nippon Kagaku Zashi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 553 (1966).

[10] T. Yamashina, *Shokubai (Catalyst)*, **9**, 9 (1967).

glass closed system of a Gulbransen type microbalance having the sensitivity of 7.21×10^{-7} g/div. (1 div.= 0.01 mm). The total volume of the system was about 1800 ml, and the system could be evacuated below 1×10^{-5} mmHg.

The rate of decomposition of i-C_3H_7OH adsorbed on nickel oxide was measured by using a vacuum apparatus having a mass spectrometer described previously.[10] The essential feature of the apparatus was the connection of the reaction vessel to a Mitsubishi MF1-T4 quadrupole mass filter by a variable leak (Granville-Phillips). Using the apparatus, the reaction mixture can be analyzed continuously throughout the course of the reaction.

Results

Effect of γ-Preirradiation on the Properties of NiO. Changes in the catalytic activity, the content of excess oxygen and the electrical conductivity of NiO were examined as a function of the preirradiation of γ-rays. The results are summarized in Fig. 2, in which the catalytic activity is the decomposition rate of the H_2O_2 at 40°C. Each value was found to change with the increase of irradiation dose. The change is remarkable when a total dose is greater than about 1×10^8 R. No distinct changes due to the irradiation were observed in the BET surface area and the X-ray diffraction pattern. In Fig. 3, the catalytic activity and the conductivity are shown as a function of the amount of excess oxygen with the irradiation. Linear relationships are seen in both cases. It must be noted that the electrical conductivity of NiO, a p-type semiconductor, was observed to decrease in spite of an increase in the excess oxygen content with the irradiation.

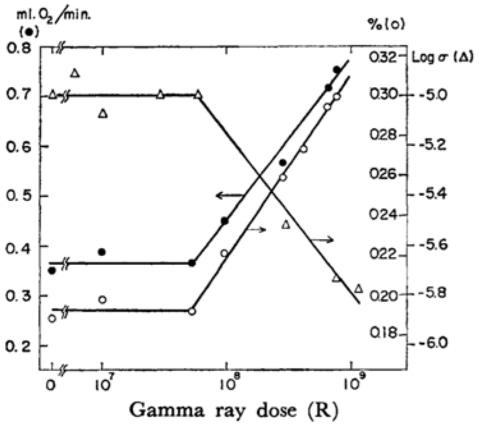


Fig. 2. Catalytic activity, excess oxygen and electrical conductivity of NiO as a function of γ-ray dose of preirradiation.
●: catalytic activity (40°C)
○: excess oxygen (iodometry)
△: electrical conductivity

Several properties of the non-irradiated and irradiated (8.8×10^8 R) NiO are summarized in Table 1.

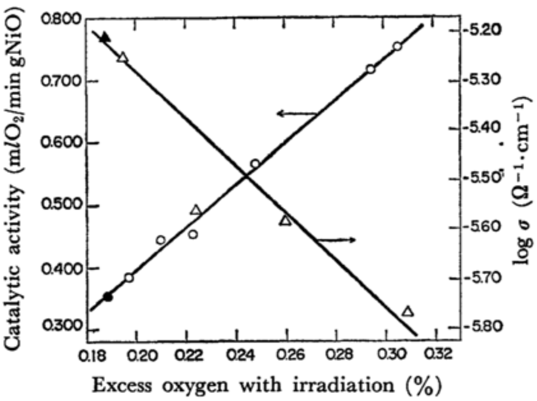


Fig. 3. Catalytic activity and conductivity *vs.* amount of excess oxygen with irradiation.
○: catalytic activity
△: electrical conductivity
●▲: non-irradiated

The anomaly observed in the relation between the conductivity and the excess oxygen content induced by the irradiation could be ascribed to the changes in the adsorption state of surface oxygen and the defect structure. The some properties of the excess oxygen have been compared on the non-irradiated NiO with the irradiated NiO; in the experiments described below, the authors have examined on two samples, NiO(I)-non-irradiated, NiO(II)-irradiated (8.8×10^8R).

Flash Desorption of Surface Oxygen. By means of a microbalance technique and by raising the temperature at a 1°C/min rate *in vacuo*, desorption curves of the oxygen from NiO(I) and from NiO(II) were obtained. The experimental results are shown in Fig. 4.

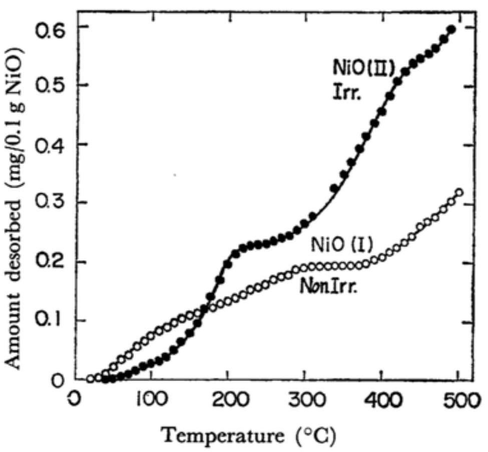


Fig. 4. Amount of excess oxygen desorbed during raising temperature (1°C/min) *in vacuo*.
○: non-irradiated NiO
●: irradiated (8.8×10^8r) NiO

TABLE 1. EFFECT OF IRRADIATION ON VARIOUS PROPERTIES OF NiO

		NiO(I) non-irradiated	NiO(II) irradiated (8.8×10^5R)
Catalytic activity (decomposition of 7.5% H_2O_2, 40°C)		0.36 (ml·O_2/min)	0.76
Activation energy (25—45°C)		11.1 (kcal/mol)	20.4
Excess oxygen	iodometric	0.188 (%)	0.305
	gravimetric	8.50 (%)	9.29
Electrical conductivity (25°C)		3.65×10^{-6} ($\Omega^{-1}\cdot cm^{-1}$)	0.965×10^{-6}
Reduction rate	by H_2 (60 mmHG, 190°C)	72 min (10% reduction)	108
	by CO (70 mmHg, 250°C)	150 min (4% reduction)	not reacted
Surface area (B. E. T.)		10.6 (m^2/g)	9.9
X-Ray diffraction (powder method)		no difference	

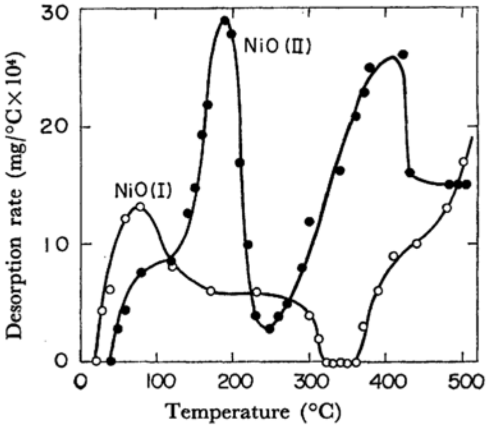


Fig. 5. Desorption rate of excess oxygen during raising temperature (1°C/min) *in vacuo*.

Further, the rates of oxygen desorption are plotted as a function of the desorption temperature in Fig. 5. As can be seen in these figures, the amount of oxygen desorbed from NiO(II) was less than that from NiO(I) in the temperature range below about 200°C, and the peaks of the desorption rate appeared at about 100°C for NiO(I) and about 200°C for NiO(II).

Changes in the electrical conductivity of the both samples during the desorption of excess oxygen are shown in Fig. 6, where log σ *versus* $1/T$ is plotted. As can be seen from the figure, NiO samples after irradiation have a lower conductivity than before, and when NiO(II) was heated up to higher temperatures *in vacuo*, a much different curve from that of NiO(I) was observed. Namely, an irregular " S " shaped change was observed for the NiO(II) in the temperature range 150—250°C. After heating up to 500°C NiO(II) became to behave like NiO(I). This fact seems to show a disappearence of the irradiation effect by the heating. The temperature of 200°C which gave the lowest conductivity in the irregular region corresponds with the temperature giving a high peak on the desorption rate curve in Fig. 5. The irregular "S" shaped curve in the conductivity-temperature relationship is a characteristic feature for the irradiated samples, and the extent of the curvature becomes larger with increasing irradiation dose.

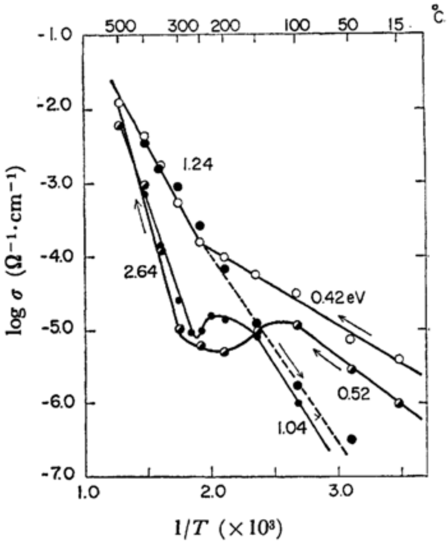


Fig. 6. Temperature dependence of electrical conductivity of NiO before and after irradiation, *in vacuo*.

○: non-irradiated sample (NiO(I))
◑: irradiated (8.8×10^8R) sample (NiO(II))
●: NiO(I) and NiO(II), cooled *in vacuo*
•: conductivity change of NiO in H_2 (2 mmHg), obtained by Dereǹ *et al.*[16]

Adsorption of CO_2. Using the vacuum microbalance, adsorption measurements of CO_2 at room temperature were carried out on NiO(I) and NiO(II). Because the adsorption was a very rapid process, comparisons between NiO(I) and NiO(II) were not possible from the kinetics of adsorption. The amount of CO_2 adsorbed during 30 min at room temperature and under the pressure of 20 mmHg was shown in Table 2. It is to be noted that the amount of CO_2 adsorbed by

TABLE 2. AMOUNT OF CO_2 ADSORBED BY NiO CO_2: 20 mmHg, AT 25°C

	NiO (I) non-irradiated	NiO (II) irradiated (8.8×10^8R)
Total amount of CO_2 adsorbed	0.0590(mg/0.1 g NiO)	0.0136
Amount of CO_2 desorbed by evacuation	0.0405	0.0063
Amount of CO_2 remained on NiO	0.0185	0.0073

NiO(II) is much less than the amount adsorbed by NiO(I). The process of electrical conductivity change during the adsorption of CO_2 at room temperature is given in Fig. 7, where the temperature at which the thermal treatments *in vacuo* were made is indicated along each curve. Conductivity changes resulted from adsorption were larger in NiO(I) than in NiO(II) in the cases of the pretreatment below 200°C.

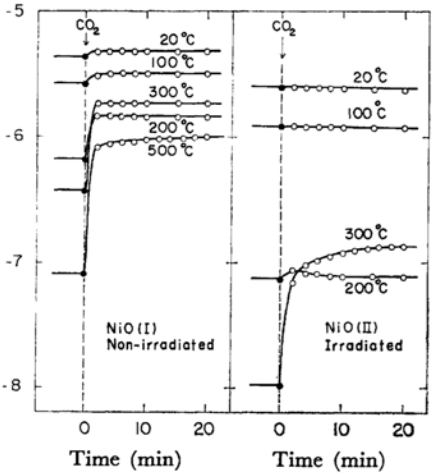


Fig. 7. Variation of electrical conductivity of NiO(I) and NiO(II) with adsorption of CO_2 (20 mmHg) at room temperature.
Sample was heated for one hour *in vacuo*, at the each temperature shown in figure, before CO_2 admission.

Decomposition of i-C_3H_7OH in Adsorbed Layer. To obtain another evidence on the reactivity of the irradiated oxide surface, the catalytic decomposition of i-C_3H_7OH by NiO(I) and NiO(II) has been examined. After i-C_3H_7OH was allowed to adsorb on the oxide at room temperature and under 30 mmHg pressure for 20 hr, the vapor of i-C_3H_7OH remained in the gas phase was removed by the evacuation at room temperature, then the strongly chemisorbed i-C_3H_7OH was desorbed by raising the temperature. The change in pressure of the system was read and the products were analyzed at every 50°C.

Results are presented in Fig. 8 and Fig. 9 where the relative intensities of main products, i-C_3H_7OH, $(CH_3)_2CO$, C_3H_6 and CO_2 are compared. With rise of desorption temperature, the

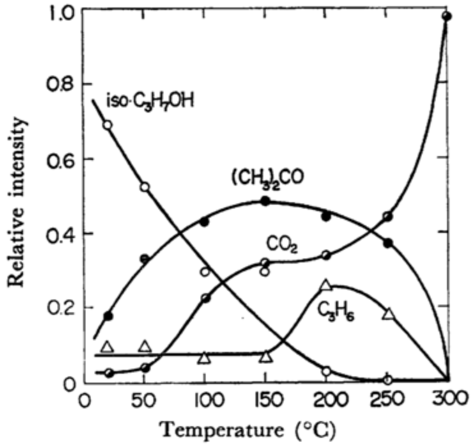


Fig. 8. Relative intensities of main products desorbed from adsorbed layer of i-C_3H_7OH, analysed by a quadrupole spectrometer; non-irradiated NiO (NiO(I)).

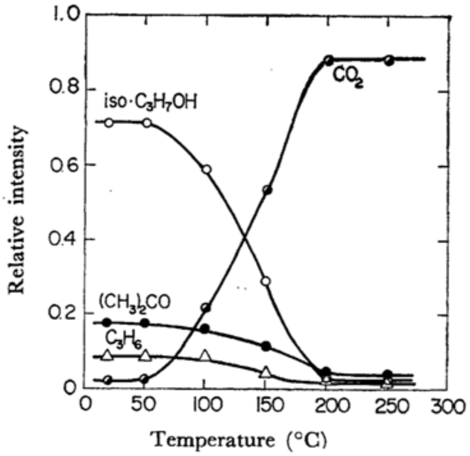


Fig. 9. Relative intensity of main products desorbed from adsorbed layer of i-C_3H_7OH, analysed by a quadrupole spectrometer; irradiated (8.8×10^8R) NiO (NiO(II)).

TABLE 3. DEHYDROGENATION OF i-C_3H_7OH ON IRRADIATED NiO
(rising rate of temperature 1°C/min, analyzed by quadrupole spectrometer)

	Non-irradiated	Irradiated (6.7×10^8R)	Irradiated (8.8×10^8R)
Starting temperature of dehydrogenation of i-C_3H_7OH	115°C	140°C	210°C
Completion temperature of dehydrogenation of i-C_3H_7OH	250	280	330

composition of i-C_3H_7OH in the products decreased and that of CO_2 increased, on the other hand, $(CH_3)_2CO$ and C_3H_6 were observed to form only in the case of NiO(I) sample. The experimental results concerning the dehydrogenation of i-C_3H_7OH on NiO(I) and NiO(II) are summarized in Table 3. It can be seen that the reaction was retarded by the irradiation.

Reductive Properties of Irradiated NiO. Reduction rates of NiO(I) and NiO(II) by H_2 and CO were measured with the vacuum microbalance. Velocity curves for the reduction by H_2 (60 mmHg, at 190°C) and CO (70 mmHg, at 250°C) are presented in Fig. 10, where the reduction rate of NiO(II) is much lower than that of NiO(I).

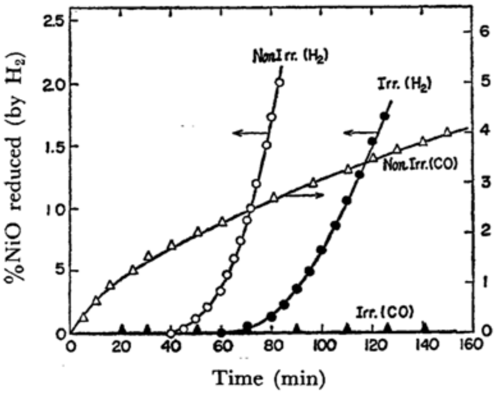


Fig. 10. Reduction curves of NiO samples by H_2 (60 mmHg, 190°C) and CO (70 mmHg, 250°C), ○△: non-irradiated, (NiO(I)) ●▲: irradiated (8.8×10^8R)(NiO(II).

Discussion

Measurements for the catalytic activity, the content of excess oxygen and the electrical conductivity of NiO as a function of γ-ray irradiation dose have shown abrupt changes when a total dose is greater than about 1×10^8 R. In the previous study on the hydrogen reduction of NiO with the irradiation,[8] the authors have found nearly the same phenomena as the present resulst. However, it is difficult at the present time to give full interpretation on the phenomena of the abrupt changes in terms of the irradiation.

In the present paper, discussion has been made on the surface state and the active sites of the irradiated NiO.

Surface State of the Irradiated NiO. Many works have been described on the surface properties of nickel oxide affected by nuclear irradiation.[11-13] Experiments by Charman and Dell[11] and Maxim and Braun[12] have shown that the amount of surface excess oxygen in NiO was increased by the reactor irradiation. The correlation between electrical properties and the content of excess oxygen of the reactor irradiated NiO has been investigated by Nachman *et al.*[13] They concluded that the complicated change in conductivity could be attributed to the radiation-induced defects in the lattice.

In the present study, the electrical conductivity was found to decrease and the amount of excess oxygen was found to increase as the irradiation dose was increased (Fig. 2). Such results can not be expected in ordinary p-type semiconductors. Therefore, the change in the conductivity seems to have no connection with the change in the excess oxygen content due to the irradiation. The descrease in the conductivity would be due to the decrease in the concentration of positive holes, *i. e.*, the charge-carriers, because the irradiation introduces deep trapping level on the vacant cation site as pointed out by several authors[13,14] in the study of nuclear radiation. According to the study by Young,[14] the conductivity of NiO was found to decrease after the nuclear irradiation *in vacuo* while to increase after the irradiation in oxygen. His results are much different from those of the present study which have shown the decrease in the conductivity after the γ-ray irradiation both *in vacuo* and in oxygen. The difference could be due to the conditions of irradiation and also the preparation of NiO samples, *i. e.*, Young prepared it by the complete oxidation of nickel foil at 1000°C.

Iodometric titration measurements with the partial dissolution method[9] have shown that the most of excess oxygen induced by the irradiation appeared to be near the surface of NiO particles. In view of the above facts, the most reasonable conclusion is that irradiation might cause two different effects against the surface properties of NiO: one is the induced chemisorption of oxygen and the other is the hole-trapping which makes to decrease in the concentration of charge-carrier. By the irradiation of γ-rays, surface excess oxygen may be converted to an adsorbed state bonding more strongly with the NiO lattice than the one before the irradiation, as

$$O^{-}_{(ads)} \rightsquigarrow O^{2-}_{(ads)}.$$

Changes in the electrical conductivity of NiO(II) during the CO_2 adsorption were much less than those of NiO(I) as shown in Fig. 7. The adsorption processes of CO_2 on the both samples could be considered as follows[3]:

---

[11] H. B. Charman and R. M. Dell, *J. Phys. Chem. Solids*, **23**, 1967 (1962); *Trans. Faraday Soc.*, **59**, 470 (1963).

[12] I. Maxim and T. Braun, *J. Phys. Chem. Solids*, **24**, 537 (1963).

[13] M. Nachman, L. Cojocaru and L. Ribco, *Nukleonik*, **10**, 1 (1967).

[14] D. A. Young. *Discussions Faraday Soc.*, **31**, 267 (1961).

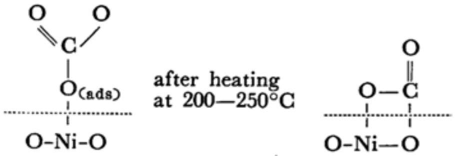
for NiO(I).

$$CO_2 + O^{-}{}_{(ads)} + Ni^{2+} = CO_3{}^{2-} + Ni^{3+} \quad (1)$$

and for NiO(II).

$$CO_2 + O^{2-}{}_{(ads)} + Ni^{2+} = CO_3{}^{2-} + Ni^{2+} \quad (2)$$

According to this mechanism, the concentration of Ni^{3+} ions in NiO(I) may be increased by the adsorption of CO_2, and the conductivity would be increased. Changes in the conductivity during the CO_2 adsorption was found to increase gradually as the pretreatment temperature was raised, and remarkable change was found above 200—250°C. This may be attributed to the change in the adsorbed state. Considering from the model proposed by Eischens *et al.*[15] and that proposed by Alexeyev *et al.*,[16] the change would be as follows:



This model requires that, after a heat treatment at higher temperature, CO_2 should become to adsorb on nickel ions which formed as a result of desorption of surface excess oxygen.

The irregular variation observed in the electrical conductivity of irradiated NiO when the temperature of sample was raised *in vacuo*, seems to be associated with the abrupt desorption of excess oxygen (Figs. 4 and 5) in nearly the same temperature range. It can be concluded that the strongly chemisorbed oxygen produced by the irradiation ($O^{-}{}_{(ads)} \rightsquigarrow O_{(ads)}{}^{2-}$) may start to desorb suddenly at 150°C. Consequently the concentration of charge-carriers (positive holes) diminished and it caused the decrease of conductivity. The phenomena of "S" shaped variation in $\log \sigma$ *vs.* $1/T$ curve have been found in the case of n-type semiconductors,[15] *e. g.*, ZnO, CdS, *etc.* Experiments carried out by Dereń *et al.*[16] on the conductivity of NiO have shown that the $\log \sigma$-$1/T$ curve in hydrogen (2 mmHg) was nearly the same as that found in the present study for the irradiated NiO (Fig. 5). The same experiments in this laboratory have given the same result as above.

The suggestion drawn from these experiments was that semiconducting property of the surface layer of NiO would be changeable from p-type to n-type. However, the clear explanation of these phenomena remains as a problem for the future.

Interpretaion of Catalytic Sites on Irradiated NiO. Many groups of workers have studied in recent years on the radiation effects on the catalytic activity of powdered catalysts. However their results have been rather conflicting and varied considerably with experimental systems and procedures. Consequently, it is very difficult to interpret the mutual relation between active sites and the surface structure changed in terms of irradiation. In the present study, the catalytic activity of NiO for decomposition of H_2O_2 was increased, while that for decomposition of i-C_3H_7OH was decreased by the irradiation. It can be concluded that active sites on NiO produced by irradiation should be different in each reaction. Considering the proportional relation between the amount of excess oxygen determined by the iodometric titration and the catalytic activity changed by the irradiation, it can be concluded that the active sites for decomposition of H_2O_2 correspond to the positive holes.

In his considerations regarding the mechanism of catalytic decomposition of H_2O_2 on NiO, Roginsky[17] has assumed that the positive holes produced by oxygen adsorption could be the acceptors of electrons from reactants. According to this assumption, the catalysts with higher concentration of positive holes would have the higher catalytic activity. The model proposed by Roginsky might be applied to the interpretation in the case of irradiated NiO.

On the other hand, the active sites for decomposition of i-C_3H_7OH, adsorption of CO_2 would not relate to the positive holes, but to the adsorption state of oxygen on irradiated NiO. Experiments on reductive properties of NiO, showed that reactivity of surface oxygen on irradiated NiO was much less than that on non-irradiated NiO.

The amount of CO_2 adsorbed by irradiated sample (NiO(II)) was only one-fourth of that by NiO(I). The nature of adsorption sites for CO_2 on NiO seems to be affected by the state of surface excess oxygen, *i. e.*, whether the surface excess oxygen is chemisorbed strongly or weakly. The adsorption measurements have shown that the ratio of the amount of i-C_3H_7OH adsorbed by the both samples at room temperature, was nearly the same as that of CO_2 at room temperature. From the above consideration, it seems to be most reasonable to conclude that the weakly chemisorbed oxygen ($O^{-}{}_{(ad)}$) might be more reactive than the strongly chemisorbed one ($O^{2-}{}_{(ad)}$) for decomposition reaction of i-C_3H_7OH. However, further clarification on the active sites produced on NiO by the irradiation must await more detailed studies.

---

15) B. M. Arghiropoulos and S. J. Teichner, *J. Catalysis*, **3**, 477, (1964).

16) J. Dereń, J. Haber and J. Sloczynski, *Bull. de L'academie Polonaise des Sciences(Série des Sciences chimiques VIII)*, 391 (1960).

17) S. Z. Roginsky, *J. Chem. Sci. Ind.*, **2**, (2) (1957).