BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3447—3450 (1969)

Effect of γ-Preirradiation on Catalytic Activity of Nickel Oxide for the Oxidation of Carbon Monoxide

Yoshisato TEZUKA and Toyosaburo TAKEUCHI
Faculty of Literature and Science, Toyama Universiy, Gofuku, Toyama

(Received July 1, 1969)

The change in NiO catalytic activity upon the variation in the irradiation of γ-rays in the presence of O_2 gas was studied. Activities were determined for the reaction of CO with NiO and for the oxidation reaction of CO on NiO. The results showed a decrease in the CO-NiO reaction rate with an increase in the irradiation of NiO, particularly in the absence of oxygen; if the irradiation was more than 7×10^7R, the reaction rate increased as both the irradiation in the presence of oxygen and the oxygen partial pressure increased. The activity change in NiO was explained by assuming the migration of the specially-active oxygen into the oxide bulk by means of the irradiation of γ-rays.

Various types of adsorbed oxygen have been proposed as the reaction intermedia of the catalytic oxidation caused by the metallic oxide. The correlation between the type of oxygen and its reactivity does not, however, bear this out clearly since the metal oxide catalytic activity is greatly affected by: (1) the treatment of the metal oxide, (2) the impurity present in the oxide, and (3) the reactant employed.

Several studies[1,2] published recently on the catalytic effects of the irradiation of γ-rays on nickel oxide have concluded that the activity of the oxide is greatly influenced by the irradiation of γ-rays; it sometimes increases and sometimes decreases. This fact indicates that the behavior of the oxygen of the metal oxide upon the irradiation is very complicated. Many areas remain unexplored concerning the behavior of the oxygen of the metal oxide

---

[1] T. Yamashina and T. Nagamatsuya, This Bulletin, **38**, 507 (1965).

[2] T. Yamashina and M. Sano, *ibid.*, **38**, 1801 (1965).

which had been subjected to the irradiation of γ-rays and the role of oxygen in catalytic reactions.

This study concerns the reactivity of the oxygen of the nickel oxide, which was irradiated with various doses of γ-rays. The reactivity was observed through the reaction between carbon monoxide and the oxygen of the oxide, and the catalytic reaction between carbon monoxide and oxygen gas.

Experimental

For each test run, 0.5g of nickel oxide was used. The nickel oxide used was obtained by igniting extra-pure nickel nitrate furnished by the Wako Chemicals Co. in an atmosphere of air at 550°C for 24 hr. The irradiation of the oxide was made in a vessel with a breaker joint, as is shown in Fig. 1. Two kinds of samples were prepared. One was the oxide which was evacuated under 10^{-6} mmHg at 300°C for 4 hr and then sealed. The other was prepared in the same manner, but after evacuation a certain amount of oxygen was admitted. The tube was pressured to 7 or 18 cmHg with oxygen. Both tubes were sealed and irradiated by ^{60}Co γ-rays. The dose rate was 5.84×10^5 R/hr. After irradiation, the samples were drawn out and kept at room temperature for about one week. The tube was then connected to the apparatus.

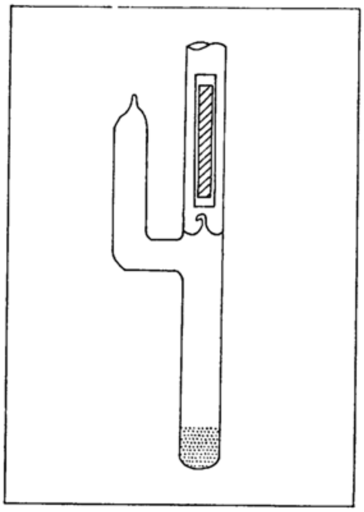

Fig. 1. The reaction vessel.

The reaction was carried out by the statistical method. The volume of the reaction vessel, including the manometer, was about 150 m*l*. In order to freeze the carbon dioxide produced by the reaction, a U-tube cooled by liquid oxygen was used to connect the reaction vessel and the manometer. Apiezon oil was used to measure the pressure decreases resulting from the reaction. Prior to use, the samples were evacuated again for about 2 hr at a temperature of 300°C to a pressure of 10^{-5} mmHg; then the temperature was lowered to the reaction temperature of 131° or 251°C. For the reaction between carbon monoxide and nickel oxide, carbon monoxide (12 cm oil) was introduced into the vessel. For the reaction between carbon monoxide and oxygen on nickel oxide, the 12 cm oil of a mixture of cardon monoxide and oxygen (mol ratio 2 : 1) was introduced into the vessel.

The oxygen used was of a commercial grade. It was purified by passing it through a trap cooled by liquid nitrogen. The carbon monoxide (purity: 99.9%) was supplied by the Takachiho Chemicals Co.

The surface areas were measured by the B.E.T. method, using ethylene at −183°C, as had been by Wooten and Brown,[3] after the test of the activity was finished.

The structure of nickel oxide was examined by a X-ray diffractometer (Rigaku Denki, Model D-3F) operated at 30 kv and 40 mA and adopting the Debye-Scherrer method.

Results

No change due to the γ-irradiation was observed in the oxide structure by means of X-ray diffraction.

The relation between the radiation dose and the B.E.T. surface area is shown in Table 1.

TABLE 1

Radiation Dose (R)	0	1.04×10^8	4.6×10^8
Surface area (m^2/g)	8.9	8.9	8.8

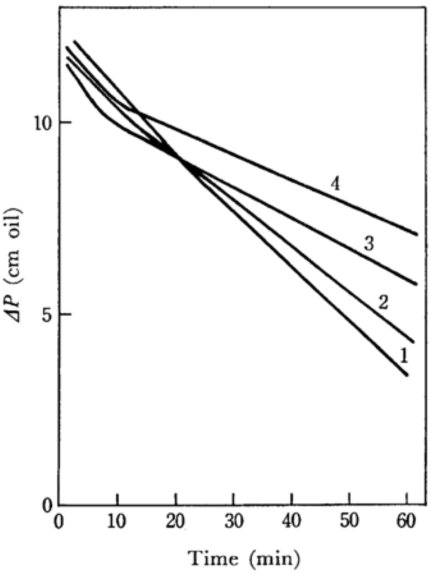

Fig. 2. The decrease of pressure of carbon monoxide on nickel oxide irradiated with γ-rays in the absence of oxygen gas.
1, no irradiation
2, 5×10^6 R
3, 7.1×10^7 R
4, 4.6×10^8 R

---

[3] L. A. Wooten and C. Brown, *J. Am. Chem. Soc.*, **65**, 113 (1943).

The results show that irradiation did not affect the B.E.T. surface area.

In the reaction of nickel oxide with carbon monoxide, the time-pressure relationship was approximately linear when the radiation dose was small. However, a curved line was given when the radiation dose was greater than 5×10^7 R and when the radiation was carried out in a vacuum. Several results are shown in Fig. 2. The rate of reaction in the latter case was determined from the slope of the linear part of the curve at the initiation of the reaction. Figure 3 shows the dependency of the radiation dose on the reaction rate. The figure shows that the irradiated oxide reaction rate is greater in the presence of oxygen than in the absence of oxygen. Also, in both cases the rate decreases with an increase in the radiation dose.

In the oxidation of carbon monoxide on nickel oxide, the time-pressure relationship was given approximately as a straight line. Figure 4 shows the correlation. The rate of reaction in Fig. 5 was determined from the slope of the line. Figure 5 indicates that the reaction rate on nickel oxide irradiated in the absence of oxygen gas decreases with an increase in the radiation dose, but the rate on nickel oxide irradiated in the presence of oxygen increases upon a radiation of more than 7×10^7 R and with increases in the pressure of the oxygen environment.

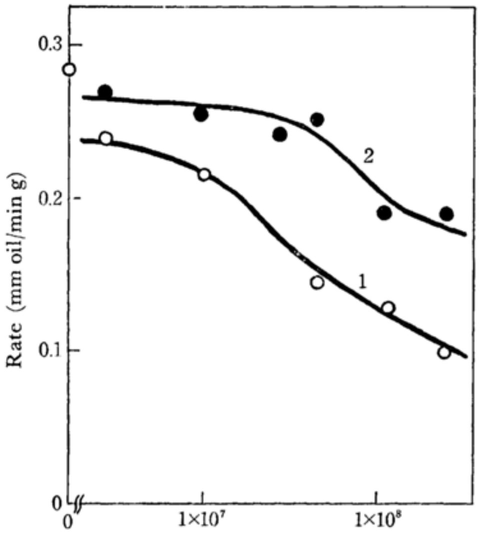

Fig. 3. The dependency of the reaction rate of carbon monoxide and nickel oxide on dose of γ-rays.
1, in the absence of oxygen gas
2, in the presence of oxygen gas (7 cmHg)

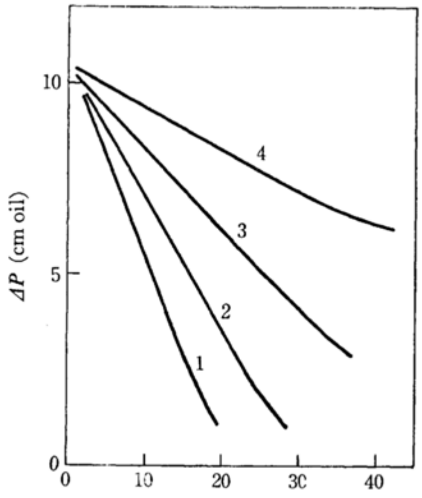

Fig. 4. The decrease of carbon monoxide and oxygen gas on nickel oxide irradiated with γ-rays in the absence of oxygen gas.
1, no irradiation
2, 5×10^6 R
3, 1.04×10^8 R
4, 4.6×10^8 R

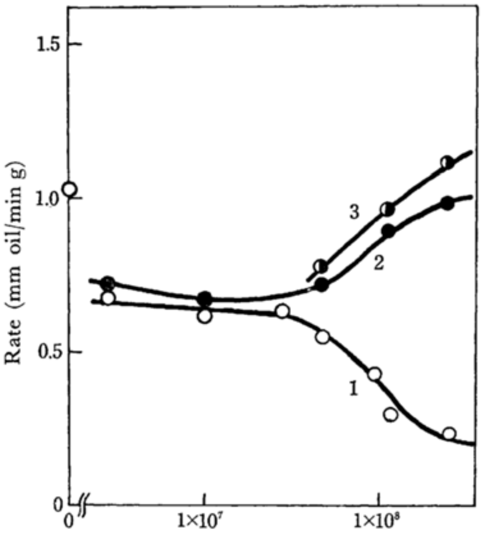

Fig. 5. The dependency of the reaction rate of carbon monoxide and oxygen on dose of γ-rays.
1, in the absence of oxygen gas
2, in the presence of oxygen gas (7 cmHg)
3, in the presence of oxygen gas (18 cmHg)

Discussion

A remarkable change was found in the catalytic reaction rate of carbon monoxide with oxygen gas on nickel oxide irradiated with γ-rays of more than 7×10^7 R in the presence (A-1) and in the absence (A-2) of oxygen. The dose which changed the rate is very similar to that reported by Yamashina[2] who studied the decomposition of hydrogen peroxide on nickel oxide irradiated in an atmosphere of air.

The rates of the reaction of nickel oxide with carbon monoxide irradiated both in the presence (B-1) and in the absence (B-2) of oxygen gas decrease as the radiation dose increases. The decrease is smaller, however, when the oxide is irradiated in the presence of the oxygen. This fact would suggest that the active oxygen on the surface becomes inactive or migrates into the interior upon irradiation. It was found that the irradiation of γ-rays promotes the migration of oxygen into the bulk of nickel oxide.[4]

Several types of oxygen have been proposed as the intermedium of the reaction on catalytic oxidation.[5-9] The oxygen which is active in the catalytic oxidation and in the migration into the bulk of the metal oxide has been considered to be charged as O^-.[10] The vacancy of the site caused by the migration of the adsorbed oxygen into the bulk during the irradiation would be replaced by another oxygen. The amount of oxygen on the surface would then be kept constant if the oxygen exists in the gaseous phase because the replacement of the adsorbed oxygen is enchanced. The almost constant reaction rate on the oxide irradiated with doses up to 7×10^7 R in the presence of oxygen (A-1 and B-1) can be explained in terms of the replacement of the adsorbed oxygen. The great rate decrease in B-1 in the area of doses of more than 7×10^7 R can be explained by assuming that the bond energy of the adsorbed oxygen changes due to the variation in the electronic property[11] of the surface, which is itself affected by the concentration of the migrated oxygen. In this study, the oxide was evacuated under 10^{-5} mmHg before the admission of carbon monoxide. The evacuation leads to a loss of the adsorbed oxygen. The amount of loss is affected by the radiation dose because the change in the radiation dose alters the concentration of oxygen in the bulk. We may expect a remarkable decrease in the bond energy of the adsorbed oxygen when the concentration of the oxygen in the bulk approaches to saturation. In consequence, the adsorbed oxygen in such a condition would desorb more readily by evacuation. Thus, the amount of oxygen remaining on the surface would be smaller. The decrease in adsorbed oxygen results in a decrease in the reaction rate, as was found when A-2 was irradiated with a dose of more than 7×10^7 R.

The small decrease found in the rates of the A-1 and B-1 reaction on the oxide irradiated with less than 7×10^7 R in the presence of oxygen can be explained similarly in terms of a decrease in the amount of adsorbed oxygen with an increase in the inner oxygen. The marked in the rate in the A-1 catalytic reaction on the oxide irradiated with more than 7×10^7 R in the presence of oxygen can not, however, be explained on only the simple assumption of the marked decrease in the amount of the adsorbed oxygen, as was done with the B-1 reaction. We assume that the irradiation of of γ-rays of more than 7×10^7 R increases the fraction of the site of active oxygen which can be desorbed readily by the evacuation; such sites would be occupied by the oxygen admitted together with the carbon monoxide.

We appreciate the help of the Japan Atomic Energy Institute in performing the irradiation tests.

---

[4] T. Yamashina and T. Nagamatsuya, *Shokubai (Catalyst)*, **9**, (4), 38 (1967).

[5] E. R. S. Winter, "Advances in Catalysis," Vol. 10, Academic Press, New York, N. Y. (1958), p. 176.

[6] T. I. Barry, "Proc. 2nd Intern. Congr. on Catalysis" (Technip., Paris) (1960), p. 1440.

[7] R. J. Kokes, *J. Phys. Chem.*, **66**, 99 (1962).

[8] K. Tarama, S. Teranishi and K. Hattori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **81**, 1665 (1960).

[9] K. M. Sancier and T. Freund, *J. Catalysis*, **3**, 293 (1964).

[10] F. S. Stone, "Advances in Catalysis," Vol. 13, Academic Press, New York, N. Y. (1962), p. 1.

[11] W. Klemm and K. Hass, *Z. Anorg. Allgem. Chem.*, **219**, 82 (1924); *cf.* G. Parravono and M. Boudart, "Advances in Catalysis," Vol. 7, Academic Press, New York, N. Y. (1955), p. 66.